The ferrox-process in an industrial scale - Developing a stabilisation process for air pollution control residues from municipal solid waste incineration

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PREFACE

This PhD thesis is the result of an Industrial PhD study prepared at Environment & Resources DTU, Technical University of Denmark and at Babcock & Wilcox Vølund ApS. Professor Dr. Agro Thomas Højlund Christensen and Associate Professor Ph.D. Dorthe Lærke Jensen acted as supervisors from Environment & Resources DTU and Senior Engineer, M.Sc. Erhardt Peter Bisschop Mogensen acted as supervisor from Babcock & Wilcox Vølund ApS. The PhD project was financed by AV Miljø, Babcock & Wilcox Vølund ApS, the Danish Academy of Technical Sciences ATV (through the Danish Industrial PhD Fellowship Programme), the EU LIFE 99-programme (LIFE 99 ENV/DK000615), I/S Amagerforbrænding, and I/S Vestforbrænding.

The PhD. project formed part of a large research programme on the Ferrox-process (the Ferrox-project). An international patent application covering the Ferrox-process was filed in 1996 and Ferrox® is a registered trademark providing exclusive right to Babcock & Wilcox Vølund ApS. Associated with this research programme are three PhD projects, of which this is one. The other two PhD projects are conducted by Mette Abildgaard Sørensen from Environment & Resources DTU and Thomas Astrup from DHI Water & Environment and Environment & Resources DTU. These studies deal with the heavy metals association to iron oxides in relation to use of iron oxides in the Ferrox-process (Sørensen, 2001) and methods for evaluation of the long-term development of environmental parameters (pH, ionic strength, etc.) in stabilised and raw APC-residues (Astrup, still under preparation). These projects have formed natural interfaces to the work presented in this thesis.

Enclosed in the PhD thesis are five journal manuscripts prepared during the PhD study:

1. Lundtorp, K.; Jensen, D.L.; Sørensen, M.A.; Mogensen, E.P.B.; Christensen, T.H. Treatment of waste incinerator air-pollution-control residues with $FeSO_4$: Concept and product characterization. Accepted for publication in *Waste Management & Research*. 2001.
2. Jensen, D.L.; Lundtorp, K.; Christensen, T.H. Treatment of waste incinerator air-pollution-control residues with $FeSO_4$: Laboratory investigations of design parameters. Accepted for publication in *Waste Management & Research*. 2001.
3. Lundtorp, K.; Jensen, D.L.; Sørensen, M.A.; Mosbæk, H.; Christensen, T.H. On-site treatment and landfilling of MSWI air pollution control residues. Manuscript submitted for publication in *Journal of Hazardous Waste and Materials.*
4. Lundtorp, K.; Jensen, D.L.; Christensen, T.H. Stabilisation of APC-residues from waste incineration with $FeSO_4$ in a semi-industrial scale. Revised for publication in *Journal of the Air and Waste Management Association.*
5. Lundtorp, K.; Christensen, T.H. The importance of pH control during treatment of municipal solid waste incineration residues. Manuscript intended for submission to *Environmental Technology*.

However, the papers are not included in this www-version but can be obtained from the Library at Environment & Resources DTU, Bygningstorvet, Building 115, Technical University of Denmark, DK-2800 Lyngby (library@er.dtu.dk).

In addition to the enclosed manuscripts, proceedings and presentations at 8 international conferences have been included in the PhD study but not in the thesis. Finally, technical progress reports prepared for the funding parties have been a part of this Ph.D. study. A translation of one chapter from the final report for the contributors is included in the thesis as an appendix.

In the thesis, references to the appendices are made in square brackets e.g. [4]. The appendices appear from the list of contents.

Thomas H. Christensen, Dorthe L. Jensen, and Erhardt P.B. Mogensen are gratefully acknowledged for their support throughout the study and for establishing the framework, which made this Ph.D. project possible. AV Miljø, Babcock & Wilcox Vølund ApS, the Danish Academy of Technical Sciences ATV (through the Danish Industrial PhD Fellowship Programme), The EU LIFE 99-programme (LIFE 99 ENV/DK000615), I/S Amagerforbrænding, and I/S Vestforbrænding are acknowledged for providing financial support. Special thanks to Mette A. Sørensen for her company and sparring throughout the project. During the work on the semi-industrial scaled plant the flexible assistance and sparring provided by Henrik Birch (DHI Water & Environment) are acknowledged. Carina Aistrup, Pernille Dühring, Heidi Dvinge, Susanne Kruse, Christel Mortensen, Herluf Riddersholm, Charlotte Scheutz, and Bent Skov, Environment & Resources DTU are acknowledged for their assistance with the comprehensive analytical work. Finally, my wife Lia is gratefully acknowledged for her support, patience, and for her caring way of telling my sons Jeppe and Tue that Daddy is working late again.

Allerød / - 2001

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Kasper Lundtorp

SUMMARY

Waste incineration is widely used for handling municipal solid waste. A disadvantage of waste incineration, however, is the residues. Especially residues from flue gas cleaning (air pollution control residues or APC-residues) are a problem due to their high content of salts and trace elements. Both are leached out when the residue is brought into contact with water. Concentrations of more than 100 g Cl/l and 1 g Pb/l have been observed. Several techniques for reducing leachability of these contaminants from residues have been developed. A new technology, the Ferrox®-process, has been suggested. Prior to this PhD project, the Ferrox-process was studied in three master student projects. The Ferrox-process is based on a mixing of residue, water and iron(II) whereby the iron precipitates as hydroxides. The added iron is subsequently oxidised in the suspension with the residues. During the process, trace elements are bound to the iron oxides, whereas salts dissolve. Finally, the water is removed and discharged as wastewater. The wastewater has a low content of trace elements, such as Pb, and a very high content of salts which are removed from the residue in this way. The APC-residues enriched with iron by the process can be washed with additional water after removing the wastewater in order to achieve a better removal of salts. The stabilised APC-residue called the Ferrox-product has low leachability of trace elements because of the added iron that immobilises the trace elements. Furthermore, the leaching of salts such as Cl, K, and Na is low as a result of the removal of these elements during the process.

This PhD project seeks to develop the Ferrox-process for full-scale application on APC-residues with focus on the impact of process parameters on the quality of the wastewater and the leaching properties of the Ferrox-product. In the analytical work focus has been on especially Pb, but also on Cd, Cr and salts. Three types of APC-residues have been used in the project: semidry APC-residue, fly ash, and fly ash mixed with sludge from a wet scrubber system.

Initially, the experimental part of the Ferox-process was studied in a laboratory scale in which the significance of a variety of process parameters on the Ferrox-product and the wastewater was examined. The result of these investigations was used for the design and erection of a plant in a semi-industrial scale (150-200 kg/treatment). The process parameters were further studied in a semi-industrial scale and scale dependent factors were identified. Evaluation of the leaching properties of the Ferrox-product was carried out continuously by a range of leaching tests. These leaching tests are more or less standardised and are based on bringing the solid material into contact with water under controlled circumstances. Subsequently, the water was analysed to determine the release of e.g. Pb from the solids. The result of leaching tests is important for determining the short and long-term properties of the Ferrox-product with regard to leaching and thereby assessing the environmental impact.

Description of the Ferrox-process can be divided into parts as follows:

- APC-residues – handling and homogeneity
- Ferrous sulphate - handling and addition
- Water
- Mixing sequence
- Iron(II)-oxidation
- pH adjustment
- Separation
- Washing

Each part is discussed separately based on the results achieved in the laboratory and in semi-industrial scale.

The properties of the APC-residues vary. The impact of this on the Ferrox-process was studied and it was found that the process is able to cope with the expected variations in the content of salts and readily available hydroxides.

Ferrous sulphate was added as a near saturated solution. To ensure precise dosage a system for on-line measurement of the Fe(II) concentration in the near saturated solution was developed. The system is based on a correlation between density and Fe(II) concentration.

The water used for mixing may either be brackish water or reused water from washing the Ferrox-product at the end of the Ferrox-process.

The amount of water and Fe(II) added during the mixing was examined. The amount of water used is less important. The amount of iron used should exceed 5 g Fe/kg fly ash and 30 g Fe/kg semidry APC-residue to ensure the lowest possible leaching from the Ferrox-product. On the other hand the amount of iron added should not be too high, because this causes a low pH in the suspension and prevents a satisfactory adjustment of pH during the process.

The added iron was oxidised in the suspension after being mixed with water and the residue. Atmospheric air proved able to oxidise the Fe(II) relatively quickly with a good Ferrox-product as result. A method to determine the concentration of Fe(II) in the suspension was developed, based on extraction with $HClO_4$. The method was used for monitoring the oxidation of the added Fe(II) in a semi-industrial scale. As a result of this study, it was found that the recommended aeration time for treatment of APC-residues on the semi-industrial scale plant is 20-50 min depending on the type of residue treated.

In the process of up-scaling the Ferrox-process from a laboratory scale to a semi-industrial scale, pH-adjustment turned out to be a necessity in order to avoid high concentrations of Pb in the wastewater. In practise the pH had to be lowered and maintained constant. Three agents for controlling pH (CO_2, $FeSO_4$, and H_2SO_4) were examined. All three were able to control pH. H_2SO_4, however, neutralises alkalinity, which is a disadvantage with regard to long-term stability of the stabilised residues. Considering the very high alkalinity of the semidry APC-residue, H_2SO_4 could safely be used for controlling pH during treatment of this type of residue. During the examination of the three pH controlling agents the content of Cd, Cr, and Pb in the water as a function of pH was studied. This resulted in a "pH window" in which the concentration of the three studied elements was low. Finally, the influence of the time that pH was maintained constant on the concentration of Cd, Cr, and Pb was examined. It was found that Cr and Pb concentrations in the wastewater were affected by the time pH was maintained stable. This result was used to determine an optimum time, in which pH was maintained in order to reduce the concentrations of Cr and Pb in the wastewater. Adjusting pH to between 10 and 11 and maintaining this pH for 30 – 60 minutes (from the pH adjustment began) yielded a satisfactory quality of the wastewater and a good stabilisation.

After oxidation and pH adjustment, the water was separated from the solids (the Ferrox-product) and thereby created a wastewater fraction that was discharged from the process. The composition of the wastewater depends on the type of residue treated and the process configuration. In a semi-industrial scale, the wastewater was proven to have a high content of salts and a generally low content of trace elements e.g. Cd, Cr, and Pb. The high content of salts was desired in order to remove these from the Ferrox-product.

In the end it is possible to wash the Ferrox-product, ensuring that salts are removed more effectively. Different aspects of washing the Ferrox-product were studied. The amount of water needed for the washing is recommended to be around 3-4 l/kg depending on the type of residue treated.

In general, the leaching properties of the Ferrox-product are not seriously affected by varying process conditions as long as the amount of Fe added does not fall below a certain level. Ferrox-products based on treatment of semidry APC-residue, fly ash, and fly ash mixed with sludge were carefully examined including a total digestion and extensive characterisation with leaching tests. It was found that the Ferrox-process had only a marginal impact on the alkalinity. Leachability of Pb from the Ferrox-product was reduced several orders of magnitude compared to the corresponding untreated APC-residue. Leachability of other trace elements, e.g. Ba, Cd, Cu, and Zn, was likewise reduced. In some studies, the release of Cr was found to be higher from the Ferrox-product compared to the corresponding untreated residue. The removal of salts,

e.g. Cl, during the process resulted in a reduced release of such salts from the Ferrox-product.

In conclusion, the Ferrox-process was developed from a laboratory scale to semi-industrial scale during this project without any major obstacles. During the project a number of scale-dependent parameters were identified. Finally, some process parameters were optimised for full-scale use of the Ferrox-process.

DANSK SAMMENFATNING

Lundtorp, Kasper (2001). The Ferrox-process in an industrial scale - Developing a stabilisation process for air pollution control residues from municipal solid waste incineration. Ph.D. afhandling ved Miljø & Ressourcer DTU, Danmarks Tekniske Universitet og Babcock & Wilcox Vølund ApS.

Affaldsforbrænding er en vidt udbredt måde at håndtere husholdningsaffald på. En ulempe ved affaldsforbrænding er de restprodukter, der dannes. Særlig restprodukter fra røggasrensning er problematiske pga. deres høje indhold af salte og tungmetaller. Begge dele udvaskes ved kontakt med vand og resulterer i meget høje koncentrationer i vandet. Koncentrationer på over 100 g Cl og 1 g Pb er iagttaget. For at imødegå problemet er der udviklet flere teknikker, som nedsætter udvaskningen af tungmetaller fra restprodukterne fra røggasrensning. En nyopfundet teknik er Ferrox®-processen, hvor restprodukterne blandes med vand og jern(II), hvorved jern(II) fælder som hydroxider. Jern(II) forbindelserne oxideres efterfølgende til jern(III)oxider ved beluftning af suspensionen. Under processen bindes tungmetallerne til jernoxiderne, hvorimod en række salte opløses. Efterfølgende skilles vandet fra og bortledes som spildevand. Spildevandet har et lavt indhold af tungmetaller såsom Pb og et meget højt indhold af salte, som derved fjernes fra restproduktet. Restprodukterne, som nu er beriget med jernoxider, kan vaskes for at udvaske yderligere salte. Det stabiliserede restprodukt kaldes Ferrox-produkt og er kendetegnet ved, at udvaskningen af tungmetaller er lav som følge af jerntilsætningen og deraf følgende immobilisering. Ydermere er udvaskningen af salte f.eks. Cl, K og Na lav, som følge af udvaskningen af disse under Ferrox-processen. Forud for nærværende projekt var Ferrox-processen undersøgt i tre projekter udført af civilingeniørstuderende.

Dette Ph.D. projekt søger at udvikle Ferrox-processen til brug i fuldskala på røggasrensningsprodukter med fokus på procesparametrenes indflydelse på spildevandets kvalitet og Ferrox-produktets udvaskningsegenskaber. I projektet er der særlig fokuseret på Pb, men også Cd, Cr og salte er betydende analytiske parametre. Der er udvalgt tre typer røggasrensningsprodukter fra affaldsforbrænding til arbejdet: Semitørt restprodukt, flyveaske og flyveaske iblandet slam fra våd røggasrensning.

Eksperimentelt er Ferrox-processen først undersøgt i laboratorieskala, hvor en række parametres betydning for Ferrox-produktet og spildevandet er undersøgt. Resultatet heraf har derefter været brugt til at designe og opstille et anlæg i semiindustriel skala (150-200 kg/behandling). I semiindustriel skala er procesparametrene yderligere undersøgt, og skalaafhængige faktorer er identificeret. Evaluering af Ferrox-produktets udvaskningsegenskaber er sket løbende med anvendelse af en række forskellige delvist standardiserede udvaskningstests, hvor vand og Ferrox-produkt bringes i kontakt under kontrollerede former med efterfølgende analyse af vandet for at bestemme

stoffrigivelsen af f.eks. Pb. Anvendelsen af udvaskningstests indgår i en bedømmelse af Ferrox-produktets udvaskningsegenskaber på kort og lang sigt.

Ferrox-processen kan opdeles i delemner og processer, som gennemgås enkeltvis med henvisning til opnåede resultater i laboratoriet og i semiindustriel skala:

- Restprodukter – håndtering og homogenitet
- Ferrosulfat – håndtering og tilsætning
- Vand
- Blanding
- Jern(II) oxidation
- pH justering
- Separation
- Vask

Restprodukternes egenskaber varierer. Indflydelsen heraf på Ferrox-processen er undersøgt og det er fundet, at Ferrox-processen kan håndtere de forventede variationer i saltindhold og lettilgængelig hydroxider.

Ferrosulfat tilsættes som en koncentreret opløsning. For at sikre en eksakt dosering er der udviklet et system til on-line måling af Fe(II) koncentrationen i den doserede opløsning. Systemet er baseret på en sammenhæng mellem densitet og Fe(II) koncentration.

Vandet, der bruges under blandingen i processen, kan enten være brakvand eller vand fra vask af Ferrox-produktet, som således genbruges.

I forbindelse med blanding af restprodukt, vand og jern(II) er vand- og jernmængderne undersøgt. Vandmængderne har kun ringe betydning. Jernmængden, der blandes med restprodukt og vand under blandingen, bør være over 5 g Fe(II)/kg flyveaske og 30 g Fe(II)/kg semitørt restprodukt, for at stabiliseringen er fuldt effektiv dvs. udvaskningen fra Ferrox-produktet er lavest mulig. På den anden side skal jerndoseringen ikke være så høj, at pH i suspensionen bliver for lav og derved forhindrer en tilfredstillende justering af pH senere i processen.

Efter blanding oxideres det tilsatte jern(II) i suspensionen. Atmosfærisk luft er påvist at give en hurtig oxidation med et godt resultat. En metode til bestemmelse af jern(II) i en suspension af restprodukt er udviklet og baseres på ekstraktion med 1 M perklorsyre. Metoden har været anvendt til at følge oxidationen af jern(II) i semiindustriel skala og derved bestemme følgende optimale oxidationstider for behandling af semitørt restprodukt og flyveaske på det opstillede pilotanlæg: 20 min. og 50 min. til oxidation ved Ferrox-behandling af henholdsvis flyveaske og semitørt restprodukt.

pH-justering viste sig nødvendig efter opskalering af processen til semiindustriel skala for at undgå meget høje koncentrationer af bly i spildevandet. I projektet er tre stoffer (CO_2, $FeSO_4$ og H_2SO_4) undersøgt som mulige tilsætninger for at kontrollere pH, hvilket i praksis er at sænke og fastholde pH. Alle de undersøgte stoffer kan anvendes, men H_2SO_4 er alkalinitetsneutraliserende, hvilket er negativt i forhold til stabiliseringens holdbarhed på lang sigt. Grundet den store mængde alkalinitet i semitørt restprodukt er H_2SO_4 alligevel anbefalet til pH justering under stabilisering af dette restprodukt. Et andet aspekt af pH justeringen som er undersøgt er indholdet af Cd, Cr og Pb i vandfasen som funktion af pH. Vandfasen udledes som spildevand fra processen. Udfra dette studie er der identificeret et "vindue", hvori koncentrationen i vandfasen af de tre nævnte elementer er lav. Endelig er tiden, i hvilken pH fastholdes, undersøgt ved at følge indholdet af Cd, Cr og Pb i vandfasen som funktion af tiden ved fastholdt pH. Det er fundet, at tiden har betydning for Pb og Cr indholdet i vandet og udfra undersøgelserne er en optimal tid, i hvilken pH er fastholdt, ligeledes bestemt. pH justering til en pH mellem 10 og 11, som blev fastholdt i 30 – 60 min. (fra pH justeringen startede) gav en tilfredstillende spildevands kvalitet og en god stabilisering.

Efter endt oxidation og pH justering separeres vand og faststof (Ferrox-produktet). Herved fremkommer en spildevandsfraktion, hvis sammensætning afhænger af restprodukttypen og den anvendte proceskonfiguration. I semiindustriel skala er der opnået et spildevand, som er kendetegnet ved et meget højt indhold af let opløselige salte og et generelt lavt indhold af sporelementer f.eks. Cd, Cr og Pb. Det meget store indhold af salte i spildevandet er ønskeligt for at fjerne de letopløselige salte fra det behandlede restprodukt.

Efter at spildevandet er fjernet, er der mulighed for at vaske Ferrox-produktet og derved opnå en forbedret saltfjernelse fra restproduktet. Forskellige aspekter vedrørende vask af Ferrox-produktet har været undersøgt. Den mængde vand, som giver den bedste vask i forhold til mængden, er bestemt til at ligge omkring 3-4 l/kg.

Generelt er det fundet, at Ferrox-produktets udvaskningsegenskaber ikke påvirkes synderligt af variationer i proceskonfigurationen, sålænge den tilsatte jernmængde ikke bliver for lav. Ferrox-produkter fra undersøgelserne i semiindustriel skala baseret på semitørt restprodukt, flyveaske og flyveaske blandet med slam fra våd røggasrensning er nøje undersøgt med en total karakterisering og omfattende udvaskningstests. Det er fundet, at Ferrox-processens indflydelse på alkaliniteten er marginal. Udvaskningen af bly fra Ferrox-produkterne er mange størrelsesordner mindre end udvaskningen fra de tilsvarende ubehandlede restprodukter. Også udvaskningen af andre sporelementer reduceres ved Ferrox-processen f.eks. Ba, Cd, Cu og Zn. Udvaskningen af Cr er i nogle undersøgelser fundet til at være højere fra Ferrox-produktet sammenlignet med det tilsvarende ubehandlede restprodukt. Ved at fjerne salte f.eks. Cl fra restprodukterne under processen reduceres udvaskningen af disse markant.

Samlet konkluderes det, at Ferrox-processen under projektet er videreudviklet fra laboratorie skala til semiindustriel skala uden større vanskeligheder. Under projektet er der identificeret en række procesparametre, som er skalaafhængige. Endelig er en del procesparametre optimeret med henblik på anvendelse af Ferrox-processen i fuld skala.

LIST OF CONTENTS

Appendices

In this thesis, references to the appendices are made in square brackets e.g. [4].

[1] Lundtorp, K.; Jensen, D.L.; Sørensen, M.A.; Mogensen, E.P.B.; Christensen, T.H. Treatment of waste incinerator air-pollution-control residues with $FeSO_4$: Concept and product characterization. Accepted for publication in *Waste Management & Research*. 2001.

[2] Jensen, D.L.; Lundtorp, K.; Christensen, T.H. Treatment of waste incinerator air-pollution-control residues with $FeSO_4$: Laboratory investigations of design parameters. Accepted for publication in *Waste Management & Research*. 2001.

[3] Lundtorp, K.; Jensen, D.L.; Sørensen, M.A.; Mosbæk, H.; Christensen, T.H. On-site treatment and landfilling of MSWI air pollution control residues. Manuscript submitted for publication in *Journal of Hazardous Waste and Materials.*

[4] Lundtorp, K.; Jensen, D.L.; Christensen, T.H. Stabilisation of APC-residues from waste incineration with $FeSO_4$ in a semi-industrial scale. Accepted for publication in *Journal of the Air and Waste Management Association.*

[5] Lundtorp, K.; Christensen, T.H. The importance of pH control during treatment of municipal solid waste incineration residues. Manuscript intended for submission to *Environmental Technology*.

[6] Translation of a chapter in the final report for the Ferrox-project Phase C. "Optimization of the Ferrox-process in a semi-industrial scale" (Environment & Resources DTU et al., 2001).

1. INTRODUCTION

In many countries, including many EU countries, Municipal Solid Waste Incineration (MSWI) is the primary waste disposal method. To reduce the amount of waste being landfilled the EU has issued a directive on the landfill of waste (The Council of The European Union, 1999) that limits the amount of biodegradeable MSW (municipal solid waste) going to landfills. By the end of 2020, no more than 35 % of MSW can be landfilled and therefore needs to be handled by an alternative method e.g. MSWI. This suggests that MSWI is becoming increasingly more widespread.

1.1 Origin of APC-residues

Waste incineration utilises energy and reduces the mass to 20-35 % and the volume to less than 10 % of the amount incinerated. In the furnace the waste is transformed into bottom ash and flue gas. The flue gas has a high content of substances that are vaporised during combustion, e.g. Cl, S, Cd, Pb, Hg and of particles. The flue gas is therefore cleaned of particles (called fly ash) and of components causing acid precipitation. In some cases, fly ash is removed in the same unit as the acid gas components or mixed with the residue from the cleaning of the acid components at the incineration plant. Some of the vaporised elements, including most of the heavy metals, condense on the way from combustion to flue gas cleaning.

Cleaning flue gas for acid components is mainly done by three methods: Dry flue gas cleaning systems, semidry flue gas cleaning systems, and wet flue gas cleaning systems.

Dry flue gas cleaning systems are based on cooling the flue gas and injecting dry lime. The cooling of the flue gas allows condensation to take place and this is facilitated by the injection of a powder, on which surface condensation will occur. Furthermore, the acid components e.g. HCl, HF and sulphur-compounds react with the injected lime to form Ca-salts and water. Lime is often injected in excess to ensure an adequate removal of the acid components. This results in a content of excessive lime in the residue from the dry flue gas cleaning systems. The amount of residue including fly ash produced by dry flue gas cleaning systems is 20-50 kg per tonne of waste incinerated (Chandler et al., 1997) and is named dry air pollution control residue or Dry APC-residue.

Semidry flue gas cleaning systems are based on cooling the flue gas and injecting a suspension of lime. By injection as a suspension, the water evaporates in the reactor resulting in a better contact between the reactants. The cooling of the flue gas allows condensation to take place and this is facilitated by the injected lime on which surface condensation will occur. Furthermore, the acid components e.g. HCl, HF and sulphur-compounds react with lime to form Ca-salts and water. As in the dry system, lime is

injected in excess to ensure an adequate removal of the acid components. Due to a better contact between the reactants, the surplus of lime injected is smaller than that of the dry system. The amount of residue including fly ash produced by the semidry flue gas cleaning systems is 15-40 kg per tonne of waste incinerated (Chandler et al., 1997) and is named semidry air pollution control residue or semidry APC-residue.

Wet flue gas cleaning systems are based on absorption of the acid components to water. The system typically consists of at least two steps, the acid and the alkaline step. In the first step water is typically sprayed into a quench tank in amounts that render HCl and HF to be absorbed, thus creating a strongly acidic solution, which is recycled and/or removed from the bottom of the tank. In the second step slightly alkaline conditions are maintained during a spraying of the flue gas in order to get a better absorption of SO_2. This kind of system normally generates two different wastewater streams. From the first step, a strongly acidic solution of primarily HCl is generated. This is neutralised and sulphide-compound is added to precipitate trace metals. Hereby, sludge containing trace metals are generated. From the second step, a solution of sulphite/sulphate is formed and precipitates as $CaSO_4$ with added Ca. The amount of fly ash and sludge produced by a wet flue gas cleaning system is 10-30 kg per tonne of waste incinerated and 1-3 kg /tonne waste incinerated (Chandler et al., 1997), respectively.

In this project it is chosen to name all the residues from the flue gas cleaning systems including the cleaning for acid components: Air Pollution Control Residues or APC-residues. This means that the term “APC-residue” includes pure fly ash, fly ash mixed with sludge from a wet scrubber system and dry and semidry APC-residue.

1.2 Characteristics of APC-residues and fly ash

In general the characteristics of APC-residues vary depending on the design of the incineration plant and the waste.

APC-residues and fly ash are typically fine grained materials with more than 95 % (w/w) of the fly ash having a diameter less than 2 mm and more than 99 % (w/w) of the dry- and semidry APC residues having a diameter less than 2 mm (Hjelmar, 1998). The saturated hydraulic conductivity is around 10^{-7} m/s for fly ash and around 10^{-9} m/s for APC residues (Chandler et al., 1997). This means that the hydraulic conductivity of the APC-residues is low with a saturated hydraulic conductivity close to clay ($<10^{-9}$ m/s).

1.2.1 Chemical composition

The composition of APC-residues, fly ash and fly ash mixed with sludge from a wet flue gas cleaning system vary due to variations in the waste incinerated and the operation of the incinerator. In Table 1.1 the content of some elements are shown for three types of residues distributed on intervals. Ca and Si are the dominating cations. Ca

originates from incineration and in case of dry and semidry systems also from the injection of lime. The main difference between dry/semidry APC-residues and fly ash can be described by seeing the dry/semidry APC-residues as a fly ash, which is diluted by the excess lime and reaction products from the acid gas cleaning. Hence the content of Cl and Ca is higher in the dry/semidry APC-residues, while the content of most other elements is moderately lower.

Table 1.1. Composition of APC-residues, fly ash and fly ash mixed with sludge from a wet flue gas cleaning system. D/SDAPC-residue is dry/semidry APC-residue including fly ash, FA is fly ash, and FAS is fly ash mixed with sludge from a wet scrubber system.

APC-residue	D/SD APC-residue	FA	FAS
Major elements > 100,000 mg/kg	Ca, Cl, Si	Ca, Cl, Si	Ca, Si
Major elements 10,000-100,000 mg/kg	Al, Ba, Cl, Fe, K, Mg, Na, Pb, S, Si, Zn	Al, Ca, Cl, Fe, K, Mg, Na, Pb, S, Si, Ti, Zn	Al, Ca, Cl, Fe, K, Mg, Na, S, Zn
Intermediate elements 1000-10,000 mg/kg	Ba, Cu, Fe, K, Mg, Na, P, Pb, S, Sb, Sn, Ti, Zn	Ba, Cr, Cu, Mn, P, Pb, Sb, Sn, Ti, Zn	Ba, Cu, Mn, P, Pb, Sn, Ti
Trace elements 100-1000 mg/kg	As, Ba, Cd, Co, Cr, Cu, Mn, Ni, Sb, Sn, Sr, Ti,	Ag, As, Ba, Cd, Cr, Cu, Mn, Mo, Ni, Sb, Sn, Sr, V	As, Ba, Cd, Cr, Hg, Ni, Sr
Trace elements < 100 mg/kg	Ag, As, Ba, Co, Cr, Cu, Hg, Mo, Ni, V	Ag, As, Cd, Co, Hg, Mo, Ni, Se, Sr, V	Ag, Co, Hg, Mo, Ni, V

Source: Chandler et al. (Table 11.11), 1997; Hjelmar, 1992; Hjelmar et al., 1990; Flyvbjerg and Hjelmar, 1997.

APC-residues and fly ash have a high content of soluble chloride species primarily $CaCl_2$ and excess lime, which will readily dissolve in contact with water. Hence in contact with water in excess the residues lose weight. According to literature, up to 65 % mass losses have been reported (Chandler et al., 1997). However, Hjelmar (1992) reported that 25 % (w/w) of a Danish semidry APC-residue and 11 % (w/w) of Swedish fly ash mixed with sludge was readily dissolved when leached at a liquid solid ratio 0-25 l/kg and 0-16 l/kg, respectively.

Due to a content of oxides of Ca, K, Na, and other metals the residues are usually highly alkaline (Chandler et al., 1997). Especially the dry and semidry APC-residues are very alkaline due to the excess lime from the flue gas cleaning. However, sorption of acidic components to the surface of the particles can give an initial acidic reaction in water before the alkaline material is released.

The acid neutralisation capacity (ANC) of dry and semidry APC-residues is generally high. Hjelmar (1992) reports of ANC values between 5.6 and 12 eq/kg determined by addition of HCl and titration with NaOH up to pH 7.0. The equivalent figures for fly ash and fly ash mixed with sludge from a wet scrubber system reported by Hjelmar (1992) are 2.5 and 4.5 eq/kg. Generally fly ash has a lower ANC.

1.2.2 Leaching in general

Leaching describes the dissolution of a solid that is brought into contact with a liquid. The liquid will then be enriched with dissolved species and is defined as the leachate. The extent of dissolved species in the leachate is governed directly by the following solid/liquid interactions:

- Dissolution
- Precipitation
- Sorption.

Dissolution, precipitation, and sorption are influenced by a number of other factors thus having a major influence on the leaching. These factors include:

- Inorganic complexing agents
- Organic complexing agents
- pH
- Ionic strength
- Redox-potential
- Temperature
- Solid diffusion.

The above mentioned reactions and factors define the extent of release of components from the solids to the liquid and can be described by equilibria equations. However, equilibria cannot always be assumed due to limited time and slow kinetics of the reactions. It is often convenient to assume that equilibrium is reached between the solids and the liquid close to the solids (LEA – local equilibrium assumption). As the release is driven by the reactions a continuous replacement of the liquid percolating through the solids will result in an increased release, hence the flow of liquid, the kinetics of the reactions, and the morphology of the solids are important. Furthermore, the total amount of liquid brought into contact with a solid sets a limit to the release by the equilibria. The total amount of liquid brought into contact with a solid relative to the amount of the solid is defined as the L/S-ratio (Liquid to Solid ratio). This is used for analysing and interpreting the release from a solid.

The practical use of studying leaching is to determine the expected release of constituents from a solid in a field situation. This could be water percolating through a deposit.

1.2.3 Leaching from APC-residues.

When APC-residues are brought into contact with water, a number of constituents are readily released to the water. The release of components varies with the type of residue and within the separate type of residue. Table 1.2 shows the maximum concentration levels in the leachate from various laboratory leaching tests and a few field investigations (Chandler et al. 1997, Hjelmar, 1992; Hjelmar et al, 1990; Hjelmar, 1998).

Table 1.2. Maximum concentration levels of contaminants in leachate from various incinerator APC-residues. D/SDAPC-residue is dry/semidry APC-residue including fly ash, FA is fly ash, and FAS is fly ash mixed with sludge from a wet scrubber system.

Interval	Unit	FA, D/SD APC-residue	FAS
10 – 1000	g/l	Cl, Ca, K, Na, Pb	Cl, K, Na
0.1 – 10	g/l	SO_4^{2-}, Zn	Ca, SO_4^{2-}
1 – 100	mg/l	Cd, Cr, Cu	Mo
10 – 1000	µg/l	As, Mo	As, Cr, Zn
< 1 – 10	µg/l	Hg	Cd, Cu, Hg, Pb

Source: Chandler et al. (Table 22.1), 1997; Hjelmar, 1992; Hjelmar et al., 1990; Hjelmar, 1998.

As can be seen from the concentration levels given in Table 1.2, substantial amounts of Ca, Cl, K, and Na are leached. Furthermore, some trace metal levels are very high, especially Pb. From FAS the concentration levels for trace elements are lower based on Table 1.2. The release of the salts is primarily governed either by availability control, e.g. Cl, or solubility, e.g. SO_4^{2-} and is to a large extent independent of pH. The release of several trace metals is highly dependent on pH and governed by solubility (e.g. Pb and Cd).

The high concentrations that can be achieved in the leachate pose a threat to the surrounding environment with regard to trace elements mobilised as well as salts. The latter due to the extreme concentrations in the initial leachate.

1.3 Practises regarding handling of APC-residues

Primarily due to leaching of salts and toxic elements, APC-residues are currently classified as a hazardous waste in most countries and disposed of in landfills. Landfilling of these residues can either be in monofills as in the Netherlands, Sweden, or Germany, in co-disposal with MSWI bottom ash as in the USA, or in co-disposal with MSW. The latter is being abolished in the industrialised countries. Some countries use some kind of stabilisation technique before landfilling, e.g. in France, Switzerland and other countries. In Germany, an increasing amount is disposed of in old mines (10,500-12,000 tonnes/year according to Chandler et al., 1997). Other special handling techniques include the residue being packed in big bags and landfilled. This technique eases the handling and reduces the leaching in the short term.

In Denmark, the practise of landfilling the APC-residues on a temporary basis was terminated by the end of 1999. From this year, residues were exported either for landfilling in Norway or for storing in old mines in Germany. This practise is supposed to be discontinued when a suitable solution to stabilising the residues has been reached in Denmark (Danish EPA, 2000).

1.4 Treatment processes

To prevent an uncontrolled release of contaminants from the APC-residues several treatment processes are available. These can be divided into four groups:

- Separation
- Solidification
- Chemical stabilisation
- Thermal treatment.

Separation is based on a removal of the potential contaminants typically by extraction with an aqueous solution, but in theory it could also be some kind of physical separation. An example could be extraction with acid with the salts and some of the easily available trace elements being dissolved and removed with the water. Separation processes yield a new waste stream, e.g. wastewater, that needs to be handled. Separation is used in full-scale in Switzerland.

Solidification is based on reducing the contact between the material and the water e.g. by reducing the hydraulic permeability or the surface area of the residues. Solidification is typically done by adding a hydraulic binder e.g. cement or bitumen (asphalt) in order to achieve a monolithic material. One major problem with using solidification on APC-residues is the washout of salts, which increases the surface and porosity and thereby reduces the effect of solidification on a long-term basis (Flyvbjerg and Hjelmar, 1997). Solidification of APC-residues is currently being used or has been used in full-scale in a

number of countries including Sweden, the Netherlands, Portugal, France, Switzerland, and Japan (Chandler et al., 1997; Méhu et al., 1999). Frequently, the solidification process is combined with either separation or chemical stabilisation.

Chemical stabilisation is based on immobilisation of the pollutants of the APC-residues by adding a reactant to form a mineral with low solubility. Suggested additives comprise phosphates, sulphides, activated carbon, carbonate, and several organic compounds. Of these the first three mentioned have been used in full-scale (Chandler et al. 1997). In a study by Mizutani et al. (2000) the addition of $FeSO_4$ in excess to MSWI fly ash and subsequently adjusting pH to approx. 10 with NaOH is studied. This was found to stabilise the fly ash with respect to four heavy metals. Generally the additives are able to bind one or more trace elements. Encapsulation of the APC-residues by addition of organic additives is also described (Chandler et al., 1997). One major problem in connection with chemical stabilisation is the costs and their inability to ensure immobilisation of all contaminants.

Thermal treatments include vitrification, fusion, and sintering, which all involve heating the APC-residue to 800 °C or more. Thermal treatment can potentially result in stabilised residue with very good leaching properties. However, thermal treatment has the disadvantages of being energy consuming and requiring sophisticated equipment leading to high costs. Furthermore, some elements will be vaporised during the process, resulting in the need for cleaning the exhaust gas and thereby creating a residue that has to be handled. Thermal treatment is used in full-scale, e.g. in Japan (Chandler et al., 1997).

1.5 The Ferrox®-process

The Ferrox-process is a stabilisation method for stabilisation of APC-residue and potentially other alkaline heavy metal polluted wastes. It combines separation and chemical stabilisation. The aim of the process is:

- To immobilise trace elements, which potentially could be released to the surrounding environment in unacceptable amounts on a short as well as a long-term basis.
- To prevent high concentrations of salts from being released to the surrounding environment.
- To achieve wastewater with a low content of trace elements in order to reduce the need for wastewater treatment before discharge to a recipient.
- To be of overall benefit to the environment with regard to the overall emission of trace elements from the process.
- To be simple with regard to technology.
- To be as inexpensive as possible without compromising the above mentioned aims.

The basic principle in subjecting APC-residues to the Ferrox-process is to extract easily soluble components e.g. Cl and at the same time bind trace elements to an iron oxide phase. This is done by washing the residues with a solution of ferrous sulphate and subsequently oxidising the added iron(II) into iron(III)oxides. When mixing iron(II) and alkaline material such as APC-residues, iron(II) is anticipated to precipitate as ferrohydroxide and is then found in the solid phase together with the APC-residue. By oxidising the added iron to iron(III)-oxides, an insoluble phase able to bind trace elements is formed. The solid phase is then separated from the aqueous phase to remove the extracted components e.g. Cl. To further enhance the removal of the easily soluble components the solids could subsequently be washed with additional water. The solid phase is defined as the Ferrox-product.

The formed iron(III)-oxides are not well defined. In Sørensen et al. (2000) and Sørensen and Bender Koch (2001) ferrihydrite is found in the Ferrox-treated APC-residue but no crystalline iron oxides e.g. hematite or goethite are observed. Furthermore, a study of transformation of the ferrihydrite on a long-term basis showed that the transformation of ferrihydrite into other more crystalline iron oxides is extremely slow (Sørensen, 2001). An example of the reaction is given by:

$$2Fe^{2+} + 4OH^- + \tfrac{1}{2}O_2 \leftrightarrow 2FeOOH + H_2O$$

Iron oxides are known to be insoluble and stable over a geological time-scale depending on the specific mineral in a broad spectrum of pH and redox conditions. Iron oxides are, for instance, found in acidic sandy aquifers in Denmark (Environment & Resources DTU et al., 2001). Only under extreme conditions, as in a traditional landfill with organic waste, a mobilisation of the iron can occur.

As it follows from the reaction, alkalinity is an important issue. During the process some of the readily available hydroxy ions are bound in iron oxides. Thereby the buffer systems of the residue are changed towards a lower pH as some of the capacity of the hydroxide-buffer is removed and the capacity of the iron oxide buffer system increases. Total ANC (acid neutralisation capacityincreases because iron(III) buffers in the ratio 3 eq acid per eq iron and consumes only 2 eq base per eq iron in the formation. The actual increase in ANC might be smaller than the ratio indicates (3/2 eq ANC per eq iron added) because some iron is not fully oxidised. Furthermore, the observed changes in ANC depend on the actual method used for determination.

Iron oxide's ability to bind trace elements is well known from geochemistry (Cornell and Schwertmann, 1996). As an example, this feature is used for treatment of heavy metal polluted water. The mechanism, which binds the trace elements to the iron oxide depends on the element and includes sorption and substitution as the dominating mechanisms. Numerous studies have been conducted on the binding of trace elements to

iron oxides including a PhD thesis (Sørensen, 2001) that also relates the study of heavy metals/iron oxide binding to the Ferrox-process. These points out that Pb is associated to the iron oxides in the Ferrox-products (Sørensen, 2001). In Sørensen (2001) it is argued that heavy metals bound by substitution will not be released unless the matrix in which it is bound dissolves. The heavy metals bound by sorption (surface complex formation) to the iron oxides can be released, depending primarily on the pH. If the pH value is below a certain level, the metals sorbed to the surface of the iron oxides will be substituted with H^+ and thereby released. Figure 1.1 shows the pH dependence of sorption of various metals to hydrous ferric oxide. Figure 1.1 also illustrates that heavy metals are not released from the iron oxide surface at a pH level above 7. Oxyanions and ligands display the opposite behaviour and CrO_4^{2-} can be bound by surface complexation to hydrous ferric oxide when pH is below 8 (Stumm and Morgan, 1996).

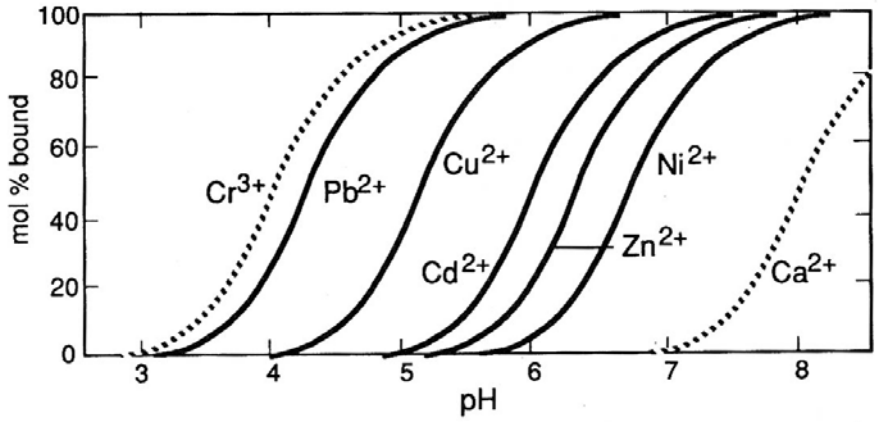

Figure 1.1. pH dependence of surface complexation of various metal ions to hydrous ferric oxide. Adapted from Stumm and Morgan (1996).

Prior to this project, the Ferrox-process was studied in three master student projects at The Technical University of Denmark (Hansen and Jensen, 1996; Lundtorp, 1996; Lundtorp; 1997). The results of these studies showed that APC-residues could be stabilised and had improved leaching properties with respect to lead, cadmium, copper, zinc and macro ions (Cl, K, and Na).

1.6 Aim and scope of the project

APC-residues are regarded as a serious disadvantage in connection with MSWI, due to the lack of appropriate means to handle these residues, and the amount in which they are produced. The Ferrox-process has been suggested for stabilisation of APC-residues from MSWI and tried out in a laboratory scale on a preliminary basis. On that background, the aim of the project is to develop the Ferrox-process for full-scale application on APC-residues with focus on the process parameters and their influence on the quality of the wastewater and the leaching properties of the stabilised APC-

residues. It is not a part of the project to document the technical devices for each unit operation as this project build on known technology in that sense, nor does it deal with the handling of wastewater, e.g. possible wastewater treatment.

Evaluating the leaching properties of the Ferrox-product is used as an approach for predicting the behaviour in a disposal scenario. Other approaches could have been used e.g. a study of the iron oxides formed and their persistency in changing conditions, but these has been excluded from the scope of this project. Specific scenarios for handling the Ferrox-product e.g. disposal or reuse are not addressed either. The work is based on the Ferrox-process without any external heating applied. The Ferrox-process in combination with some kind of thermal treatments (described in Sørensen, 2001) is therefore not considered, but should be considered as a possible supplement to process described under this project.

Based on the description of APC-residues, the analytical work, focused on lead in particular, but also on Cd, Cr, and major ions e.g. Cl. Organic pollutants such as dioxins have not been included in this project, one of the reasons being that release of this type of pollutants from residues has not yet been recognised as a problem in the EU. Hence, the framework for assessing the risk from dioxins and other organic pollutants has not been evolved. Furthermore, the potential threat from the trace elements and salts means that a stabilisation method should at least be able to cope with these elements, following which a potential threat from organic pollutants could be included. The high salinity in general makes it difficult to apply ordinarily used modelling tools e.g. MINTEQA2. Special modelling tools for solutions with high salinity exist e.g. Phreeqpitz, but the application of such tools is outside the scope of this project.

2. EXPERIMENTAL APPROACH

2.1 Experimental strategy

The experimental approach sets out to establish knowledge in a laboratory scale about a number of important process parameters and their influence on the quality of the wastewater and the leaching properties of the stabilised APC-residues. This is called the laboratory phase. The knowledge achieved in the laboratory phase is subsequently utilised for designing a plant for Ferrox-stabilisation in a semi-industrial scale/pilot scale. In the semi-industrial scale, process parameters are further investigated, and documentation on the quality of the wastewater and the leaching properties of the stabilised APC-residues is established. Finally, knowledge of the technical implications of full-scale use of the Ferrox-process is established. The part of the project, which is connected to the semi-industrial scale study, is called the pilot-scale phase.

During the laboratory phase, a number of process parameters were studied ([1], [2], and [3]). However, the scale limits the process parameters that can be studied meaningfully. Examples are the rate of oxidation of Fe(II) and washing of the solids, which are very dependent on the equipment used for the process. Furthermore, some factors are scale dependent. For some it is related to the relatively larger surface in a smaller scale compared to a larger scale, e.g. carbonation during the process and temperature changes. Therefore, conclusions on process parameters based on the laboratory studies in [1] and [2] mostly serve to uncover potential problems and the influence of certain process parameters on the leaching properties of stabilised residues. The conclusions from [1] and [2] also set a starting point for the studies in the semi-industrial scale. An example of this is the washing of the stabilised APC-residue on the filter at the end of the process. This was studied in [2] and was found to yield a better Ferrox-product and therefore subsequently adopted in the semi-industrial scale process.

In the pilot phase, the process parameters can be studied in a more comparable scale to a full-scale application ([4], [5], and [6]). The study reveals the potential of using technical equipment especially designed for the purpose e.g. the aeration/oxidation equipment. Furthermore, the larger scale compared to the laboratory phase makes it possible to assess scale dependent factors e.g. temperature changes and carbonation during the process. Carbonation during the process is probably one of the reasons why pH was at an adequate level during the process in the laboratory without any addition of a pH controlling agent as opposed to the findings obtained in a semi-industrial scale. The pilot phase terminates with a final evaluation of the performance of the Ferrox-process, incorporating all the findings made during this project and with a comprehensive evaluation of the resulting Ferrox-product and wastewater. This final

evaluation serves as a documentation of the Ferrox-process in a semi-industrial scale and is described in [4].

In order to cope with variations in the composition of the APC-residues, the pilot scale phase is based on a large number of individual stabilisations run batch-wise. Each stabilisation had its own purpose e.g. investigating a specific parameter, but it also contributed to the documentation of the robustness of the Ferrox-process.

Evaluation of the results during the project are primarily based on the quality of the wastewater with regard to trace elements and on the leaching properties of the Ferrox-product with respect to salts and trace elements on a short as well as a long-term basis. Evaluation of the leaching properties is discussed below.

During the project, three types of APC-residues were studied: Semidry APC-residue, fly ash, and fly ash mixed with sludge from a wet scrubber system. Semidry APC-residues and fly ash mixed with sludge have been chosen because they represent two commonly used flue gas cleaning techniques. In many ways, dry APC-residue is comparable to semidry APC-residue and was therefore left out of the project. Pure fly ash has been included in the project because many MSWI facilities are able to handle fly ash and acid gas cleaning products separately. This means that if it was established that the Ferrox-process was not capable of stabilising combined APC-residue satisfactorily, treatment of the fly ash alone could still be an option.

2.2 Leaching tests

The Ferrox-process aims at reducing the release of trace metals and salts from APC-residues, and it is therefore important to evaluate the leaching properties. It is not possible to perform real time and full-scale leaching under realistic field conditions because of the time scale and other factors, including temperature, precipitation, and channelling. Therefore, the leaching properties are evaluated by a range of leaching tests that are more or less standardised for this purpose. These tests may have different objectives, e.g. some aim at simulating field conditions, some are for regulatory purposes, some for comparison, etc. In this project a selection of leaching tests has been used for:

1. Simulation of field scenarios
2. Comparison with results described in the literature
3. Comparison with regulatory limits
4. Comparison of untreated and Ferrox-treated APC-residues.

Re 1. For field scenario simulation, a column test was used. A column test makes it possible to evaluate the initial release from a material equal to a leaching at low L/S-ratios (0.1 l/kg) at conditions (pH, redox conditions etc.) close to those expected in a

field situation. The test does not account for channelling, variations imposed by changing seasons etc. Not included in this Ph.D. project, but in connection to it, lysimeters were established for a more comprehensive study of the leaching properties of the stabilised and untreated APC-residues under field conditions. Presently no results from this study are available.

Re 2 and 3. For this purpose a two-step batch compliance test was used. As regards regulatory limits no comparison is included in the project because the regulatory limits and the type of tests used in national legislation differ. However, the possibility for a future comparison with regulatory limits exists, as the two-step batch compliance test is expected to be adopted by legislation in the EU.

Re 4. For these purposes both a column test, a two step batch compliance test, and a pH static test were employed. In both the column test and in the two-step batch compliance test, pH is controlled by the solid phase. To some extent, it is rendered feasible to assess possible changes in the pH of the material imposed by the Ferrox-process. In a field situation, a change in pH imposed by a treatment of the APC-residues is expected to be very important in the short-term with respect to the release of trace elements. In the long-term, the buffer capacity of the carbonate system and other buffer systems are more likely to be controlling pH and the release of trace elements. In the pH static test, impact of a possible change in pH is ruled out which makes it possible to assess the importance of pH as a controlling parameter and to evaluate the release without having to account for the impact of the pH. Furthermore making pH static tests at different pH values establishes knowledge of how the material leaching properties will be affected by changes in pH. The latter being important as pH is expected to change in a field situation due to carbonation and other reactions, which are difficult to simulate in leaching tests.

By using a wide selection of leaching tests, better overall knowledge of the leaching properties of the Ferrox-product is established. This knowledge is the basis for a prediction of the long-term behaviour of the Ferrox-product with respect to leaching.

2.3 Sampling strategy

2.3.1 APC-residue

Sampling APC residues from the incinerators may either be a representative sample or a spot sample. The choice of sampling method depends, to some extent, on the purpose of the sampling. Taking a representative sample from an incinerator requires sampling over a long period. In connection with the Ferrox-process this poses a problem because the residue might change properties when stored for a longer period due to carbonation and other reactions. Therefore spot sampling was used in order to ensure a sample,

which is very similar to fresh APC-residue. Furthermore, regardless of the variations in the APC-residues, the Ferrox-process is supposed to ensure stabilisation in an industrial scale where variations may also occur. The characteristics of a spot sample of APC-residue can be compared with the characteristics described in the literature for the same type of APC-residue. Thus there is every likelihood that the spot sample has the most common features of the specific type of residue.

2.3.2 Ferrox-product

When an APC-residue has been stabilised, the resulting Ferrox-product has to be characterised, e.g. by a leaching test. Sampling of a Ferrox-product made in a laboratory scale poses no problem as the total batch can easily be homogenised. In a semi-industrial scale or an industrial scale, homogenisation is difficult to handle. In this case spot sampling might be used. In the studies described in [6] of the Ferrox-process performed on the semi-industrial scale, plant sampling from a plate-and-frame filter press was studied. It was found that there are some minor variations when sampling in different spots in the plate-and-frame filter press. As a result, sampling in the studies performed on the specific semi-industrial scale plant was always done in the same spot in which the study revealed the highest leaching of salts.

2.4 Mass balances

Mass balances were set up for the process in the study performed in a semi-industrial scale [4]. Mass balances are used to ensure that all streams in and out of the process are accounted for and to have an additional check on the analytical work. Table 2.1 shows, as an example, the mass balance for the treatment done in [4] on each type of APC-residues (SD and FA) with respect to dry matter, water, Pb, and Cl. The figures are based on masses measured during the pilot-plant experiment, determination of dry matter content and contents of Pb and Cl in the dry matter and aqueous phases. The water used for washing of the treated material on the filter press was recycled for use in the following batch. The mass balance fitted within 6 % for dry matter, which is considered to be acceptable. The balance for water fitted within 3 %, without accounting for the loss of water during aeration. The balances for Pb and Cl fitted within 7 % and 22 %, respectively. These balances are generally considered acceptable as they are imposed both by the deviations in the balances for water and dry matter and by the determination of the elements during the analytical work.

Table 2.1. Mass balance for a stabilisation of APC-residue on the pilot-scale plant with respect to dry matter, water, Pb and Cl. SD is a semidry APC-residue, FA is a fly ash and FAS is a fly ash mixed with sludge from a wet scrubber system.

		Dry matter[1]	Water[2]	Pb	Cl
SD					
In	kg	203	1150	0.85	29.8
Out with Ferrox[3]	kg	150	133	0.79	0.2
Out with water[4]	kg	66	987	0.00003	31.1
Balance	Δ%	6	- 3	- 7	5
FA					
In	kg	192	977	1.16	12.5
Out with Ferrox[3]	kg	150	132	1.10	0.2
Out with water[4]	kg	31	833	0.00001	13.9
Balance	Δ%	- 6	- 1	- 5	13
FAS					
In	kg	189	1080	1.18	9.8
Out with Ferrox[3]	kg	158	123	1.22	0.6
Out with water[4]	kg	28	937	0.00002	11.4
Balance	Δ%	- 2	- 2	3	22

[1] Including dissolved salts.
[2] Including the reused water but excluding dissolved matter.
[3] Including the residual water in the residue after treatment.
[4] Excluding the water that is removed with the moist residue after treatment.

2.5 Temperature, conductivity and pH

In the Ferrox-process, APC-residue and water are mixed, the overall sum of the processes taking place during this act is exothermic. Also, the sum of the processes taking place during the aeration/oxidation and pH-adjustment is overall exothermic. This was observed during the studies [1]-[6]. During the studies performed in a semi-industrial scale [4]-[6] the increase in temperature became more prevalent due to relatively smaller surface of the suspension in a large scale.

The increase in temperature poses a problem in measuring pH and specific conductivity. In a laboratory scale, the temperature of the suspension of residue during treatment equilibrates with the room temperature during the process. Therefore, no special precautions need to be taken in measuring specific conductivity and pH in the laboratory experiments.

In a semi-industrial scale, the temperature during the process rises from approx. 15 °C to 25-30 °C and 34-42 °C for treatment of fly ash/fly ash mixed with sludge and semidry APC-residue, respectively. In a semi-industrial scale, the impact of the changes in temperature needs to be considered when measuring specific conductivity and pH.

The specific conductivity is temperature dependent and temperature dependency varies with the composition of the solution. In this project, measuring conductivity is used for monitoring the washing of the Ferrox-product. The temperature at the beginning of this process is high (25-40 °C) and decreases to approx. 15 °C in the end. It is therefore difficult to account for the variations in temperature. As it is important to get an exact measurement at the end of the washing (see the following chapter where different aspects of the washing is discussed) the apparatus is calibrated at 15 °C with compensation to 25 °C. Thereby an inaccuracy is expected when the temperature differs from the calibration temperature (the readout is expected to be 10 – 20 % higher than the actual conductivity at 25 °C due to the higher temperature). In the event of a high temperature and high conductivity occurs simultaneously an exact value for the specific conductivity cannot be obtained directly.

The temperature also affects the pH measurements and the impact varies with the composition of the solution (Clesceri et al., 1998; Lide, 1992; Skoog et al., 1988). It is therefore difficult to obtain exact pH measurement throughout all stages of the process due to temperature variations. Exact measurement of pH is important at the end of the pH adjustment (explained in the following chapter), when the temperature is generally high, but with relatively small deviations. It is chosen to handle the problem by calibrating the pH at approx. 15 °C. The variations imposed by the temperature and other factors (high salinity, high concentrations of Na, etc.) are then determined by measuring samples at both operating temperature (25-40 °C) and calibration temperature during the experiments made in a semi-industrial scale. The temperature dependency of pH is then estimated to +0.3 pH units per 20 °C increase. This figure is slightly higher than that of a hydrogencarbonate/carbonate buffer in the same temperature range and only half of that found in a saturated $Ca(OH)_2$ solution (Lide, 1992). As the deviations in the operating temperature are modest it has been chosen to express pH in this project as the pH measured at operating temperature. The choice is based on expectations for how the calibration of pH and measuring is supposed to be done in full-scale and to overcome the variations in other factors besides temperature e.g. salinity, Na concentration. The pH values obtained and used in the project are therefore sufficient for inter-comparisons, but to get the exact pH a compensation for the temperature has to be made. In most cases, the compensation of pH during treatment of semidry APC-residues is +0.3 pH units and during treatment of fly ash/fly ash mixed with sludge +0.2 pH units can be used.

3. SEMI-INDUSTRIAL SCALE APPLICATION OF THE FERROX-PROCESS

This chapter will provide a step by step description of the Ferrox process and focus on the technical use of the process in full-scale. Furthermore, some issues related to applying the Ferrox-process into full-scale will be discussed. In brief, the Ferrox-process comprises mixing of ferrous sulphate, water, and APC-residue followed by an aeration of the added iron. After aeration a pH adjustment takes place followed by a reaction time. Finally, the suspension is filtrated and subsequently washed. The emissions from the process are a wastewater and a treated residue called the Ferrox-product. The chapter is divided into the sections listed below:

- APC-residues – handling and homogeneity
- Ferrous sulphate - handling and addition
- Water
- Mixing sequence
- Iron(II)-oxidation
- pH adjustment
- Separation
- Washing

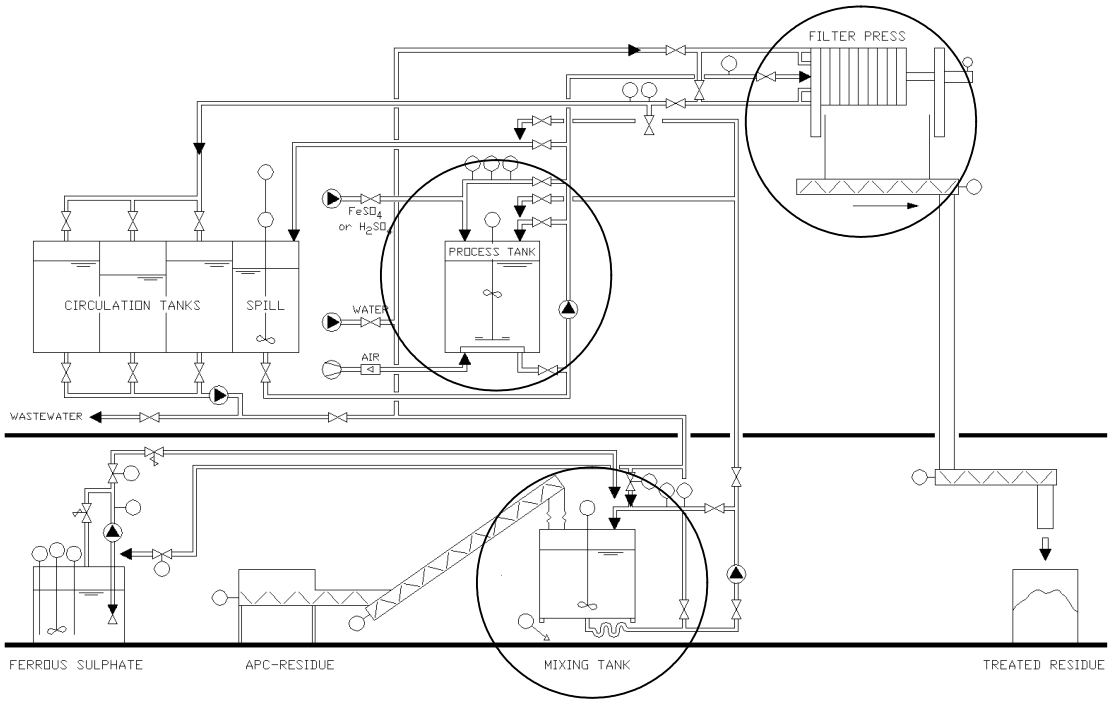

Figure 3.1. Drawing of the semi-industrial scale plant for Ferrox-treatment of APC-residues described in [4]. The three major units (marked with circles) are the mixing tank, where ferrous sulphate solution, recycled water and APC-residues are mixed, the process tank, where oxidation of ferrous iron takes place followed by pH adjustment with either additional $FeSO_4$ or H_2SO_4 and the plate-and-frame-filter press, where the treated residue is dewatered and then washed. The volume of the process tank is approx. 1.5 m^3.

The sections listed can be related to a plant for treatment of APC-residues. Figure 3.1 illustrates a semi-industrial scale plant as described in [4]. The first 4 sections relate to the mixing tank (see Figure 3.1) and to adjacent components (ferrous sulphate tank and APC-residue silo). Iron(II)-oxidation and pH adjustment takes place in the process tank and separation and washing is done in the filterpress (see Figure 3.1).

3.1 APC-residues – Handling and homogeneity

The following section provides an outline of some safety and environmental issues concerning APC-residues as well as the importance of the variations in the APC-residue properties. In a plant similar to the one depicted in Figure 3.1, APC-residue is added to the process in the mixing tank (see Figure 3.1).

3.1.1 Safety and environmental precautions

When handling APC-residues, especially from dry/semidry systems or dry fly ash, special precautions must be taken to protect the environment and working environment. The major problem is dust emission, arising from the handling of the fine-grained materials. It is important to consider this when designing a treatment plant. Prior to treatment, the dry APC-residues are stored in a silo in connection with the treatment facilities and added to the plant by a screw conveyor. Similar equipment is already in use at the incinerator plants where APC-residues are stored in a dry and humidified environment prior to transportation and further handling. Humidified residue is difficult to handle because it will stick to the equipment and eventually block any moving parts, e.g. the screw conveyor.

At a treatment plant for the Ferrox-process the dry residue is added to a tank with water and ferrous sulphate. It is crucial that this tank is tightly sealed to safeguard against dust emission. However, as hydrogen can be produced when the residues are mixed with water, the tank should also have sufficient ventilation of its headspace to avoid the danger of explosions. Several techniques exist for solving this problem. One solution could be to ventilate the headspace and use the air for the aeration of the process tank. This requires that the process is run continuously.

After the residue is added and stirred into a suspension, the problems of dust emission are eliminated throughout the remaining steps of the process.

3.1.2 APC-residue for treatment in an industrial scale

The properties of the APC-residues vary due to variations in the waste and the operation of the incinerator. A stabilisation with the Ferrox-process should be able to cope with these variations without reducing the quality of the Ferrox-product or a substantial increase of the content of trace elements in the wastewater.

Three properties of the APC-residues that could vary will be discussed here:

1. The content of readily available hydroxide
2. The size of the particles
3. The content of salts.

Re 1. In order to precipitate iron(II) in the process and to achieve the desired pH, as described later in this chapter, easily available hydroxide must be present or added. Easily available hydroxide is not well defined, but in order to execute the process within a reasonable timeframe, the hydroxide used in the process should be released within a couple of minutes. The Ferrox-process provides for a high pH level to be achieved in the mixing by means of the dosage of iron(II) (see the section about the amount of iron(II) added during the mixing). Subsequently, an accurate dosage of a pH-controlling additive is added during the pH adjustment and in this way variations in the content of the specific APC-residues of easily soluble hydroxide are accounted for. As described, the residues used in the studies [1]-[6] all had a sufficient amount of hydroxide for coping with the variations. If the content of available hydroxide is lower than the necessary amount for precipitating the iron(II) added during mixing, it can be handled in two ways: Addition of more residue during the mixing, which decreases the ratio of iron(II) added for each tonne APC-residue (this is discussed in the section about the amount of iron(II) added during the mixing), or addition of a base which ensures a precipitation of the added iron(II). No conclusive findings have been made in relation to the latter option.

Re 2. No conclusive findings have been made in treating very coarse APC-residues. In the study described in [4], [5], and [6], the untreated semidry APC-residue used was sieved through a mesh of 1 cm openings, thereby ensuring a diameter of less than 1 cm on the smallest cross section of the particle. Ferrox-treatment of this semidry APC-residue was performed with a satisfactory result [4]. This suggests that rough crushing may produce residue, which can be treated with a satisfactory result. Very large particles will potentially cause problems at a treatment plant, e.g. clogging of pipes, damaging sensors and propellers.

Re 3. A study of the washing of the treated residue performed in [6] shows that a major part of the salts are removed from the residue with the wastewater, and that the removal of the remaining salts during washing is most effective initially with a decreasing removal rate. Therefore, the variations of the initial content of easy soluble salts of the residue will only have a marginal impact on the content of easy soluble salts of the treated residues. In more than 50 treatments in the pilot-scale plant described in [4], the specific conductivity of the washing, water at the end of the washing was 10 mS/cm or less. According to the study of the washing [6], this is approximately the point where further washing only will have a marginal effect. So in none of these more than 50

batches the content of salts varies in a way where actions had to be taken to ensure the removal of salts during the process. An example of the impact on the variation in the salt content of APC-residues can be seen from the following. A figure of the net removal of K during four successive stabilisations of a semidry APC-residue and four successive stabilisations of a fly ash can be set up (Figure 3.2). The figure is based on the work presented in [4] and accounts for the K removed with the wastewater and washing water and the K added with reused washing water from the preceding stabilisation. For comparison, the amount of K leachable at L/S 10 l/kg from the resulting Ferrox-products is included. It appears that the net amount of K removed varies, primarily due to variations in the properties of the APC-residue. The leachable amount of K is insignificant in comparison and fairly constant, which indicates that despite changes in the APC-residue, the impact on the Ferrox-product is marginal.

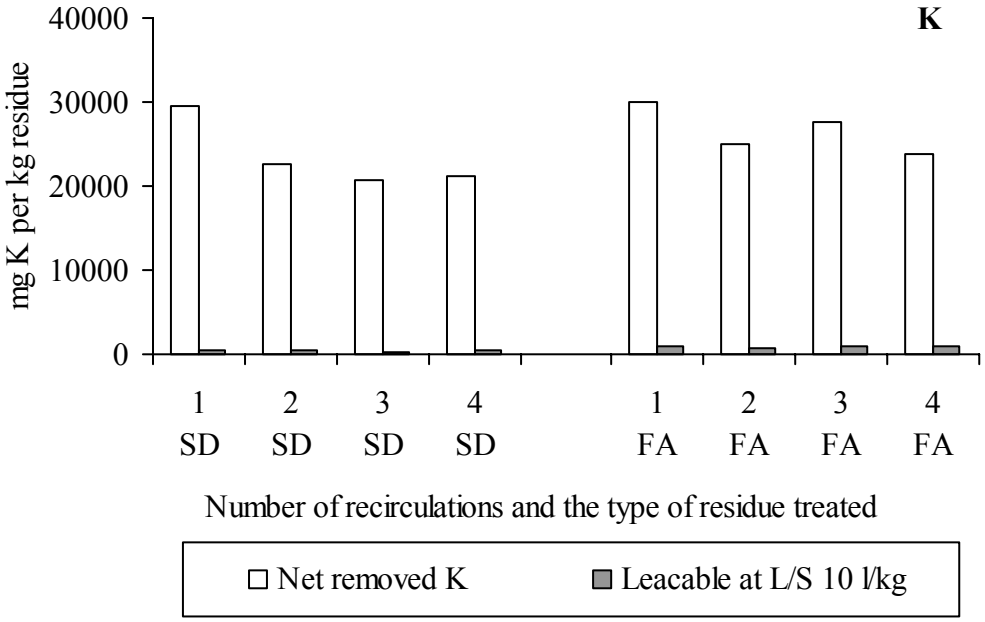

Figure 3.2. Net removed K during successive treatments of a semidry APC-residue and a fly ash and the leachable amount of K from the resulting Ferrox-products.

Another aspect of the variations of salts involves their impact on the solid-water equilibrium of many trace elements. However, as the variations do not imply noteworthy changes in the concentrations of the wastewater it will not affect the trace metal concentrations in the wastewater substantially. Comparing the wastewater from treatment of semidry APC-residue and fly ash as done in [1], [3], and [4] shows that despite the difference in concentration of Cl, the concentrations of Pb and Cd, which both form complexes with chloride, are on the same level.

Overall variations in the characteristics and hence in the behaviour of the residues are expected. However, the process is able to cope with these variations based on experience gained so far.

3.2 Ferrous sulphate - handling and addition

The Ferrox-process is based on the addition of ferrous sulphate. In a plant similar to the one depicted in Figure 3.1 the ferrous sulphate is added in the mixing tank and in some cases also in the process tank. In the following section the ferrous sulphate handling and adding techniques are discussed.

Ferrous sulphate heptahydrate ($FeSO_4 \times 7H_2O$) is a waste product arising from titanium extraction. It is widely used for wastewater treatment, and techniques for handling this chemical are known and available. The chemical will agglomerate into a solid mass if stored dry. Therefore a technique is adopted from wastewater treatment technology, under which the chemical is dumped into water when arriving to the treatment facility. Dissolving $FeSO_4 \times 7H_2O$ is an endothermic process. This technique was used in the pilot-scale plant described in [4] and shown in Figure 3.1, with solid ferrous sulphate being added in excess to a tank with water (the ferrous tank, see Figure 3.1). In this tank solid ferrous sulphate is present at the bottom with a saturated or near saturated solution above. This solution is added to the process when addition of iron(II) is required. When removed, some of the solution water is added to compensate for the solution taken out. Hereby some of the solid ferrous sulphate dissolves to reach a near saturated or saturated solution again. The solution has a pH around 1-2 due to the presence of small amounts of sulphuric acid in ferrous sulphate of technical grade. The acid conditions prevent iron(II) from being oxidised.

When using a near saturated solution for storing and adding iron(II) in a technical scale the quantity used has to be considered, especially when treating a semidry residue. In the study performed in [4] 4.9 % iron (w/w) was used for treatment of semidry residue. If the concentration of the solution is 7 % (w/w), then 700 kg of ferrous solution has to be added per tonne semidry APC-residue treated.

One of the main issues when using the technique of adding iron(II) as a concentrated solution is to ensure an exact measurement for the addition of iron(II). The added iron(II) solution is near saturated and will therefore have a concentration of approx. 5-8 % (w/w) iron(II) depending on the temperature, equilibration time, stirring and other factors. Measuring the temperature and correlating it with the solubility of ferrous sulphate at different temperatures is not viable due to the presence of impurities, e.g. sulphuric acid that changes the solubility of ferrous sulphate and to the kinetic of dissolving ferrous sulphate, which is slow at near equilibrium in relation to a technical use. A correlation between the density and the concentration as % (w/w) of ferrous sulphate can be established on the basis of figures available in chemical works of reference (Meyer and Pietsch, 1932; Hellwege et al., 1977; Stephen and Stephen, 1979) assuming a linear regression. Figure 3.3 shows the correlation from two references. From the figure it appears that the correlation is near linear at a constant temperature

and the assumed linearity is adequate compared to the desired accuracy. This correlation can be used for on line measurement of the iron(II) concentration, given that on-line density measurement devices exist and are commonly employed. One of the techniques for measuring density is based on a correlation between the density and the retention of a radioactive beam that radiates through a cross section of a pipe through which the ferrous solution is led. When applying this technique of correlating density and ferrous sulphate concentrations, temperature variations need to be considered. Figure 3.4 shows the temperature dependency of the density (data from Meyer and Pietsch, 1932). The correlation between density and temperature can be assumed linear in this case and the slope is 0.0004 kg/l per °C. From Figure 3.3 it appears that 0.0004 kg/l equals 0.013 % (w/w) iron(II). Hence the impact of variations in temperature can be estimated to 0.013 % (w/w) iron(II) per °C and can therefore be ignored in most cases. As an example an accuracy better than 1.1 % (equal to ±0.065 % (w/w) on the iron(II) concentration) can be achivied when the temperature varies with ± 5 °C and the concentration of iron(II) is above 6 % (w/w). Generally speaking, the temperature needs to be considered if the temperature in the ferrous solution varies to an extent that could compromise the desired accuracy.

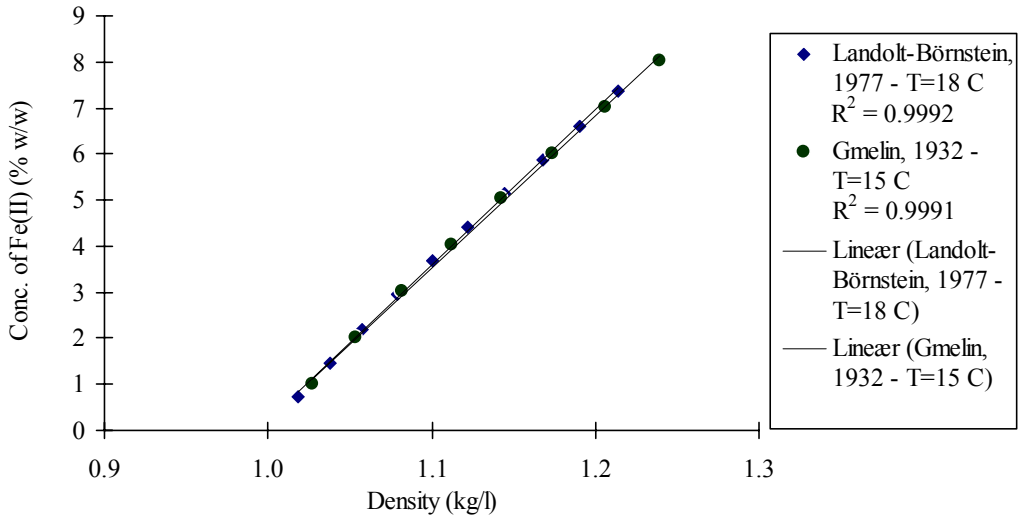

Figure 3.3. The correlation between the concentration of iron(II) and density for solutions of $FeSO_4$ from two chemical works of reference: Landolt-Börnstein (Hellwege et al., 1977) and Gmelin (Meyer and Pietsch, 1932).

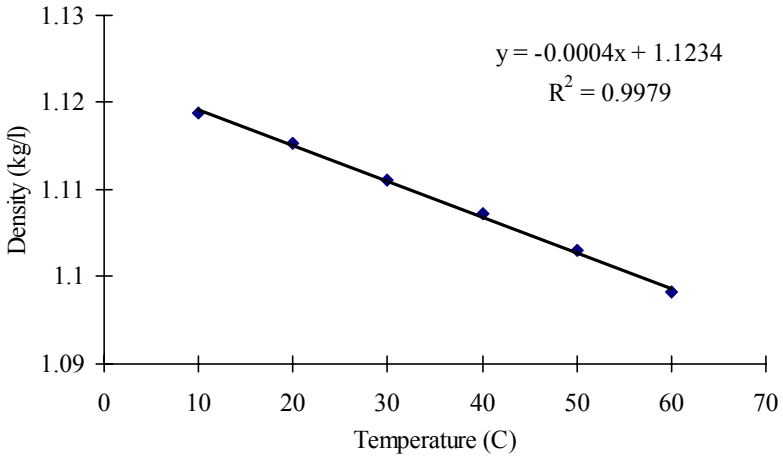

Figure 3.4. The correlation between temperature and density for a solution of 20 % (w/w) $FeSO_4 \times 7H_2O$ equal to 4.02 % (w/w) iron(II) from Meyer and Pietsch (1932).

On-line measurement of iron(II) using the correlation between density and the concentration of the ferrous sulphate solution has been used in the studies performed in [4], [5], and [6]. During these studies, an apparatus based on retention of a gamma ray processed into density was used. It was calibrated by reading the density from the apparatus and simultaneously sampling and measuring the iron(II) concentration (w/w) for approx. 20 samples with different concentrations of iron(II). Then a conversion formula giving the relationship between the density and iron(II) concentration (w/w) was calculated and entered into the apparatus so that the iron(II) concentration (w/w) was read out directly. An example of a calibration curve is shown on figure 3.5. As can be seen the correlation is good. The apparatus was calibrated once every three months, which proved the method to be very stable.

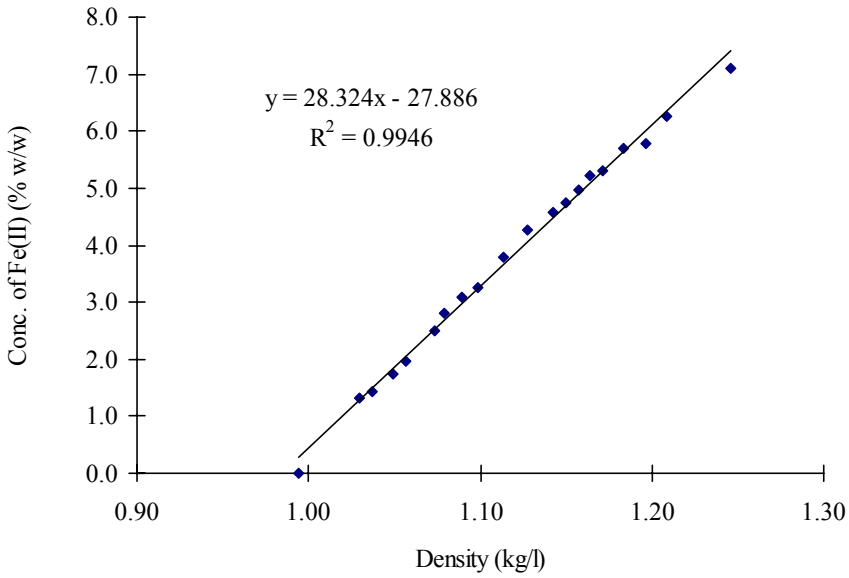

Figure 3.5. An example of a calibration curve for the density meter. The iron(II) concentration (w/w) versus density of the solution. The temperature varied between 17.3 °C and 20.9 °C and is therefore neglected.

3.3 Water

Water can be added at three points in the treatment process:

- For preparation of the concentrated ferrous sulphate solution.
- For mixing with concentrated ferrous sulphate solution and APC-residue.
- For washing the treated residue.

At a plant similar to the one depicted in Figure 3.1 water would enter the process in the ferrous sulphate tank and in the plate-and-frame filter press. The latter would be reused and reenter the process in the mixing tank (see Figure 3.1).

The water used for making the near saturated ferrous sulphate solution should be fairly clean of substances that could cause precipitation to an extent that would affect the density/iron(II) concentration measurement or build up in the system. Water with a high alkalinity should therefore not be used as this would cause precipitation of the iron(II). However, water with minor impurities e.g. lightly contaminated groundwater could presumably be used.

The water used for mixing with ferrous sulphate and APC-residue can be of low quality. It is possible to use brackish water for the mixing. This has been done in [2], in which it was found that such use has no impact on the salt removal or on the leaching properties of the stabilised residues. Alternatively, it is possible to reuse the water used for washing the treated residue after separation for the mixing. As a result, water consumption is reduced by up to 50 % [4]. This has been studied or used in [2], [4], and [6]. No impact on the removal of salts by reusing the water from the washing was detected in the studies presented in [2] and [6]. In the study presented in [4] an increase in the specific conductivity was observed when comparing a wastewater from a stabilisation with and without reuse of the washing water for the mixing (these results are not included in [4]). The increase was approx. 20 mS/cm and 10 mS/cm for treatment of a semidry APC-residue and a fly ash, respectively. In the studies of reusing the washing water for the mixing done in [4] and [6] the conclusions were that this can be done without a significant deterioration in the quality of the Ferrox-product (see also Figure 3.2 in the section about variations in the APC-residue).

After aeration and filtration, the residue is washed in order to ensure good salt removal as proven in [2]. The water used for this purpose should have a low content of salts depending on the demand for salt removal.

3.4 Mixing sequence

In the following section topics are discussed related to the first step in the Ferrox-process where water, ferrous sulphate, and APC-residue are mixed (See Figure 3.1 –

mixing tank). This means that the ingredients are added separately, but leave this step as slurry.

The sequence of mixing ferrous sulphate, water and APC-residue has been studied in [2]. It was observed that the sequence of mixing has no significant impact on the leaching properties of the treated residues. Mixing water and residues with the subsequent addition of ferrous sulphate yielded higher concentrations of Pb in the wastewater. However, this study was performed before pH adjustment and reaction time were put into practise as described in [4], [5], and [6], so the impact of the mixing order on the wastewater could be different when running the process with pH adjustment and reaction time. There are some technical aspects of the mixing sequence. On a large scale it is probably not practical to mix the dry residue and the dry ferrous sulphate before adding water as done in [2] due to the difficulties related to handling dry ferrous sulphate and residue. Based on these findings the preferred sequence of mixing is: a solution of ferrous sulphate is prepared with subsequent addition of the dry residue as described in [1], [3], and [4]. This order of mixing has been used in a semi-industrial scale in the study performed in [4] with good results.

3.4.1 Amount of iron(II)

In the mixing sequence, ferrous sulphate is added. The amount of ferrous sulphate added is limited partly by the available hydroxide in the residue and partly by the leaching properties of the residues treated. The added iron(II) precipitates with hydroxide. Therefore, enough hydroxide has to be available. If iron(II) is added in excess the pH could be too low for a proper control of pH during the process (see the section about pH adjustment). Furthermore, a major running cost with the process is the ferrous sulphate, and the use should therefore be as low as possible without compromising stabilisation. The amount of iron(II) added is studied in [2]. In this study it is found that if the amount of iron(II) added is too low, stabilisation will be insufficient. Table 3.1 shows the result of a pH static batch leaching test performed at pH 9 (the Table is modified from table 1 in [2]). From this it can be seen that for semidry APC-residue more than 30 g iron(II) per kg semidry residue is needed to ensure low leaching of especially Cd from the treated residue. For fly ash more than 5 g iron(II) per kg fly ash residue is needed to ensure low leaching of especially Cd from the treated residue.

Table 3.1. The concentration of Cd, Cr, and Pb in a single batch leaching test at a steady pH 9 and an L/S ratio of 10 l/kg from APC-residues stabilised with varying amounts of iron(II). SD is a semidry APC-residue and FA is a fly ash.

SD	Amount Fe(II) g/kg residue	Cd µg/l	Cr µg/l	Pb µg/l	FA	Amount Fe(II) g/kg residue	Cd µg/l	Cr µg/l	Pb µg/l
	20	160	430	1100		5	15	1700	12
	30	25	44	5.9		10	7.7	1700	5.6
	40	1.9	16	2.0		15	7.8	1900	3.6
	50	5.0	100	< 0.1		20	6.3	1500	2.8
	75	4.6	160	4.7		25	6.1	1400	3.8
	100	1.0	30	28					

Using 49 g iron per kg semidry APC-residue, 20 g iron per kg fly ash, and 13 g iron per kg fly ash mixed with sludge during treatment in a semi-industrial scale was well documented [4] with respect to the leaching properties of the treated residues and the wastewater composition and was found to be satisfactory. Of these amounts, 49 g iron per kg semidry APC-residue, 12.5 g iron per kg fly ash, and 12.5 g iron per kg fly ash mixed with sludge were added during the mixing. The remaining iron(II) was used for pH adjustment (described later). These amounts were chosen from the preliminary studies in the semi-industrial scale plant described in [4].

3.4.2 Amount of water

The amount of water used for mixing should be adequate to ensure easy handling of the suspension. In the studies made in [1] and [3] L/S ratios of 3 l/kg and 5 l/kg, respectively, were used successfully. In [2] L/S 2 l/kg was found to be too low for running the Ferrox-process in a laboratory scale due to practical problems. In a technical scale it would probably be possible to overcome the difficulties of handling suspensions with a low L/S ratio. However, in reality the amount of water added for the mixing is governed by the amount used for washing the treated residue due to reuse of the water used for washing. This is demonstrated in [4] where L/S-ratios between 2.7 l/kg and 3.9 l/kg were obtained.

3.4.3 Technical aspects

During mixing it is useful to monitor pH in order to make sure that all iron(II) is precipitated as indicated by a high pH. If needed, addition of more APC-residue or base can then be used to ensure a high pH by the end of the mixing. Monitoring a suspension of APC-residue poses a problem as it tends to stick to equipment such as sensors. Monitoring directly in the tank where the mixing takes place has a number of disadvantages with respect to reliability, security, and maintenance. A solution is to make a monitoring circuit where slurry is pumped out of the tank continuously and back into the tank passing a pH sensor on the way. This has been done on the equipment described in [4]. Mixing water and APC-residue yields heat and the temperature rises

during mixing to approximately 25 and 30 °C for mixing in fly ash/fly ash mixed with sludge and semidry APC-residue, respectively. When handling slurries at L/S ratios of 3-5 l/kg, adequate stirring must be added to ensure good mixing. Furthermore, it should be able to keep the slurry relatively homogeneous in order to prevent problems when emptying the tank. Care should be taken when designing pipes and pumps to prevent slurry from settling in pipes or clogging valves.

3.5 Iron(II)-oxidation.

The second step in the Ferrox-process is the oxidation of the added iron(II) after mixing. At a plant similar to the one depicted in Figure 3.1, oxidation would take place in the process tank (see Figure 3.1). The oxidation process is discussed below as are the means of determining iron(II) in the suspension.

The added iron(II), which presumably precipitates as ferrohydroxide, is oxidised as a part of the treatment. The design of the vessel for aeration of the suspension is essential to the rate of the oxidation. Therefore, determining the exact iron(II) oxidation rate in a laboratory or in a semi-industrial scale is of minor relevance. However, it is important to have a rough overview of the quantity of the added iron(II) that can be oxidised during the process and the oxidation rate to be be achieved. This will provide an estimate of the performance of an industrially sized vessel for oxidation at a plant for the Ferrox-process.

3.5.1 Oxidising agent

For the oxidation of iron(II) compounds, several oxidising agents are available. In the studies described in [1]-[6], oxygen from atmospheric air was used with a satisfactory result. Other agents such as pure oxygen, hydrogen peroxide can potentially be used, but this is not described nor studied. Considering a dosage of 50 kg Fe(II) per tonne semidry APC-residue from which 80 % is oxidised the consumption of pure oxygen is 5.7 kg (stoichiometric ratio) similar to 4400 l pure oxygen or 21000 l atmospheric air. Using the oxygen from atmospheric air is an appealing option because it is readily available, it reduces the overall consumption of resources seen from an environmental point of view, and it is relatively simple seen from a technical point of view. As atmospheric air contains 21 % (vol.) oxygen, oxidation with atmospheric air will require more energy for the blower than the use of an oxidising agent seen from a local point of view. Based on these considerations, only oxidation with atmospheric air is included in this study.

3.5.2 Determination of iron(II) oxidation

In order to monitor the oxidation of iron(II) a method for determining the iron(II) in a suspension of residue, water, and ferrous sulphate has to be thought out. In aqueous

solutions determination of iron(II) is well known and performed on a routine basis. One method which was available to this project was a technique based on extraction with 5 M HCl, where iron(II) is extracted from the solids into an aqueous phase and then measured by common laboratory techniques (spectroscopy after complexation with ferrocin). This method is used for sediments and soils (Heron et al., 1994). An extraction with 6 M HCl has been tried out on a suspension of APC-residue and ferrous sulphate with little success. Varying the concentration and amount of HCl proved to be unsuccessful as well. During extraction, iron(II) was either not extracted or oxidised in an uncontrolled manner indicating that techniques developed for sediments and soil cannot automatically be applied on residues. In this case, the behaviour indicated that other redox active components than iron were released. In [5] and [6] release of Cr is discussed and found to be dependent on time. This suggests that a suspension of Ferrox-product is not in equilibrium with respect to redox conditions, and it is therefore difficult to establish an exact scientifically based method for the determination of iron(II). Therefore "trial and error" iteration was used as an approach for developing a suitable extraction method. This resulted in an extraction with1 M $HClO_4$ being added in a ratio of 4:1 to a sample of Ferrox-products in suspension and shaken for 30 minutes before separation by filtration. $HClO_4$ is chosen because it is a strong acid (Kofstad, 1987), with low affinity for complexation with metals (unlike Cl^-) (Kofstad, 1987) and with suitable redox-properties. Despite its thermodynamic properties, $HClO_4$ reacts extremely slowly as an electron acceptor (Kofstad, 1987) and is thereby almost redox neutral during extraction. This technique yielded consisting results as shown in Figure 3.6 and discussed below. The amount of iron(II) oxidised shown in Figure 3.6 is determined with the described extraction and shown as a function of time during oxidation of a fly ash and two semidry APC-residues. The extraction method has some disadvantages:

- The small sample size compared to the total volume (approx. 20 ml was sampled) could be a problem for getting a representative sample. Eleven of the samples depicted in Figure 3.6 were subsequently also extracted by 7 M HNO_3 and analysed on a flame atomic absorption spectrophotometer. The total iron extracted in this way was consistent within 10 % for all eleven samples, which indicates the uncertainty derived from the sample size. This potential uncertainty has to be considered when evaluating the result for a single sample. However, a large number of samples will compensate for the uncertainty of the small sample size.
- There is no direct certainty for extracting all iron(II) by applying this method. However, given the coherence in the results (see Figure 3.6 and the discussion below) and the fact that the results correspond with the amount of iron(II) initially added (it is found that up to 85-90 % of the added iron(II) is oxidised), it is likely that all iron(II) is extracted. Furthermore, in the study performed by Sørensen et al. (2000) on residues treated with the Ferrox-process no crystalline iron(II) containing compounds was found. Such crystalline compounds would have the potential of withstanding the extraction with 1 M $HClO_4$.

In general, the use of the extraction method based on $HClO_4$ is regarded as being adequate because it shows a progression of the oxidation and gives a rough estimate on how much iron(II) added during mixing can be expected to be oxidised.

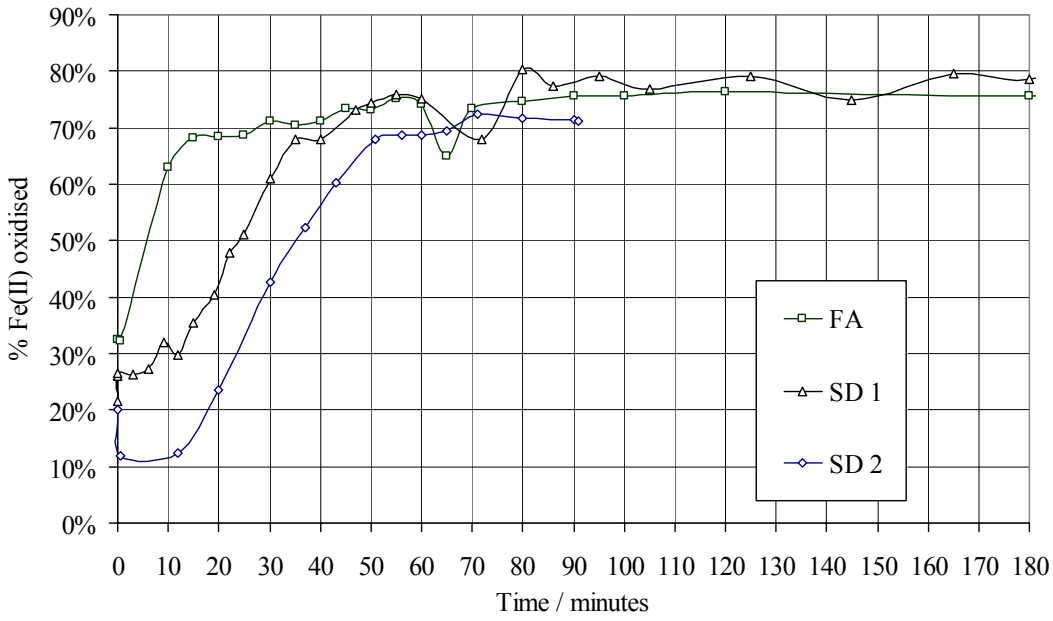

Figure 3.6. The amount of iron(II) oxidised relative to the amount added during mixing shown as a function of time during Ferrox-treatment of two semidry APC-residues (SD 1 and SD 2) and a fly ash (FA). The study is described in [6] and was carried out on the semi-industrial scale plant described in [4]. The starting point (0 minutes) denotes the time, at which aeration in the process tank started.

3.5.3 Technical aspects

Oxidation of the ferrous compounds formed during the Ferrox-process is recommended to be done in the suspension. An alternative could be to oxidise the wet solids after filtration, but the diffusion of gas through such a material is slow. In the laboratory it has been tried to oxidise the wet solids spread out in a 5 cm thick layer. After 3-4 days the solids changed colour to reddish brown indicating that oxidation had set in. In suspension this occurred within 4-6 hours in the laboratory and within 10-20 minutes on the semi-industrial scale plant described in [4]. Oxidation of the solids after separation is therefore not considered feasible. Exceptions could be if, for some other reason, heating is applied on the wet solids before oxidation or oxidation of the added iron is not required. This was not studied.

The design of a vessel for dispersion of gas into liquids or slurries is important. It is important that the slurry has as long contact time with the gas as possible and with the largest possible contact area. The first point is ensured by designing the vessel higher

than a regular tank and by the design of the stirring aggregate e.g. position of the stirrer, shape of stirrer, baffles on the tank and speed of rotation. The second point is done by dispersing the gas into fine air bobbles in the slurry. These requirements are met by equipment that includes a fast rotating device. A fast rotating device is unsuited for operating in a very inhomogeneous suspension similar to the conditions during the mixing. Hence, the requirements in the design render it difficult to mix residue, ferrous sulphate and water in the same vessel as the one, in which aeration takes place.

Figure 3.7. The tank used for oxidation at the semi-industrial scale plant described in [4] (marked with an ellipse). The height of the tank is 2.2 metres without rack. The ladder leads up to the plate-and-frame filter press seen on top of the rack.

The oxidation process was studied in a semi-industrial scale in [6]. The oxidation was done in a 2.2 m high tank with a diameter of 1 meter equipped with a fast rotating stirrer (675 rpm) and air-inlet at the bottom (65 m^3/h) shown in Figure 3.7. Figure 3.6 shows the amount of iron(II) oxidised relative to the amount added during mixing as a function of time during oxidation of a fly ash and two semidry APC-residues. From this figure it appears that oxidation almost stops when 68 % of the added iron(II) is oxidised. This is reached after 15 minutes and 40-60 minutes for fly ash and semidry APC-residue, respectively. With FA and SD, 1 the experiment depicted in Figure 3.6 continued for 24 hours resulting in oxidation of approx. 90 % and 85 % of the iron(II) added during mixing. From Figure 3.6 it also appears that part of the oxidation has taken place before the actual oxidation in the process tank started. The deviation between the two experiments on the oxidation during treatment of semidry APC-residue (SD 1 and SD 2) from Figure 3.6 could be the result of variations in the residue as the experiments were

carried out on two different batches. Furthermore, it appears that the determination of iron(II) in the suspension is useful for evaluating the progression of the oxidation, but not accurate enough for evaluating a single sample within a few percent. Oxidation of iron(II) during treatment of fly ash and sludge was not studied. However, observations made during the studies in a semi-industrial plant described in [4] and [6] revealed that the suspension shifted colour from black to brown after 10-20 minutes of aeration, which is similar to the observations made during treatment of fly ash. In the study described in [4] 20 minutes and 50 minutes were used with a satisfactory result for treating fly ash/fly ash mixed with sludge and semidry APC-residue, respectively. During this time, the temperature increased 1-5 °C in the suspension.

3.6 Adjusting pH

The third step of the Ferrox-process is to adjust pH in the slurry after oxidation and to maintain it for a certain time. This step is typically done immediately after the oxidation and in the same vessel. On a plant similar to the one depicted on Figure 3.1 pH would be adjusted in the process tank (see Figure 3.1). In the following section pH adjustment is discussed with an emphasis on the consequence for Cd, Cr, and Pb in wastewater.

When APC-residues are mixed with water, some alkaline salts, especially CaO, are dissolved, which causes an increase in the pH of the water. Some of the hydroxide is bound during the mixing with ferrous sulphate but it is ensured that there is surplus of hydroxide before aeration in order to maintain a high pH level at the beginning of oxidation. pH is the major parameter controlling release of several trace elements including Cd and Pb, when APC-residues are brought into contact with water. In such a case, the concentration of Cd will normally be controlled by $CdCO_3(s)$ and $Cd(OH)_2(s)$ and therefore the concentration of Cd will decrease at a high pH (Chandler et al., 1997). The concentration of Cr will also decrease if pH is high (Chandler et al., 1997). Pb has an amphoteric behaviour so that at a high pH high concentrations of Pb can be observed (Kofstad, 1987). The latter is a potential problem during the Ferrox-process because pH values above 12 have been observed. During the preliminary studies at the semi-industrial scale plant described in [4], concentrations up to 80,000 μg/l were observed in the water. This water, which eventually is discharged as wastewater from the process, would then need extensive cleaning before discharge. In studies done in laboratory scale described in [1], [2], and preceding studies the concentration of Pb never exceeded a few hundred μg/l. The reason for this is that the pH was lower during the process (between 10 and 11). Hence, pH depends partly on the scale. Probably the relatively large surface and the longer aeration time in connection with carbonation was responsible for the lower pH in the laboratory scale. To avoid unacceptable concentrations of lead, pH must be controlled.

If pH is altered, the equilibria between species in the water and on the solids change. So when a desired pH is reached and maintained the concentrations in the water will equilibrate with the solids. The pH will normally have to be lowered to reach the optimum pH as described above in order to reduce the Pb concentrations in the water and thereby minimise the need for wastewater treatment. However, care should be taken to avoid an uncontrolled increase of the concentration of other components, e.g. Cd and Cr if pH becomes too low. In [5] and [6] a study was done to uncover the possibilities of adjusting/controlling pH and identifying an advantageous pH, where the concentrations of Cd, Cr, and Pb are as low as possible.

Three different agents were studied:

- CO_2
- $FeSO_4$
- H_2SO_4

CO_2 reacts with hydroxide and forms carbonates, which is regarded positive with respect to long term stability. Calcium carbonate buffers the leachate at a slightly alkaline pH, which is advantageous with regard to trace metal release.

$FeSO_4$ is already used during mixing with residue and water. Therefore it is readily available and has also proven to be beneficial for the stability of the treated material. It reacts with hydroxide and forms ferrous hydroxides, which are subsequently oxidised.

H_2SO_4 neutralises hydroxide, whereby acid neutralisation capacity is reduced.

Other chemicals might be used, but no experience exists and other chemicals have not been included in this study.

These three compounds were added stepwise with the simultaneous sampling of the water at different pH values during treatment of semidry APC-residue, fly ash, and fly ash mixed with sludge. The relationship between pH and the concentrations of Cd, Cr, and Pb was thereby established. This type of experiment is based on the assumption that near equilibrium is reached for the elements studied within the 10 minutes that each pH value was maintained. If this assumption does not hold, a distinction between a development in the concentration caused by an ongoing reaction or a change in pH cannot be made directly. In order to verify this, a supplementary experiment needs to be performed, in which the relationship between time and the concentrations in wastewater at a constant pH are established.

The temperature of the suspension increased slightly 0-10 °C by adding a pH adjusting agent during the studies made in a semi-industrial scale [4]-[6]. However, the changes in the temperature mainly take place at the beginning of the pH adjustment. The

temperature during the pH adjustment is approx. 25-30 °C and 34-42 °C for treatment of fly ash/fly ash mixed with sludge and semidry APC-residue, respectively. The measured pH deviates, therefore, slightly from the actual pH, which is 0.2 to 0.3 pH units higher than the measured pH. For use in this project and in [4]-[6] this is of minor importance as it is the inter-comparison that is the main issue. Furthermore, the pH values found in this project are considered to be easier to apply in a full-scale Ferrox-process.

3.6.1 pH

Figure 3.8 illustrates the result in which either $FeSO_4$ or H_2SO_4 has been added during treatment of semidry APC-residue, fly ash, and fly ash mixed with sludge. Figure 3.8 is based on results described in [6]. All three agents were able to control pH and thereby the content of Cd, Cr, and Pb in the water. Cd, Cr, and Pb behaved almost similarly regardless of the agent used for adjusting and controlling pH. However, the assumption that near equilibrium was reached for Cr was not fulfilled, as described later.

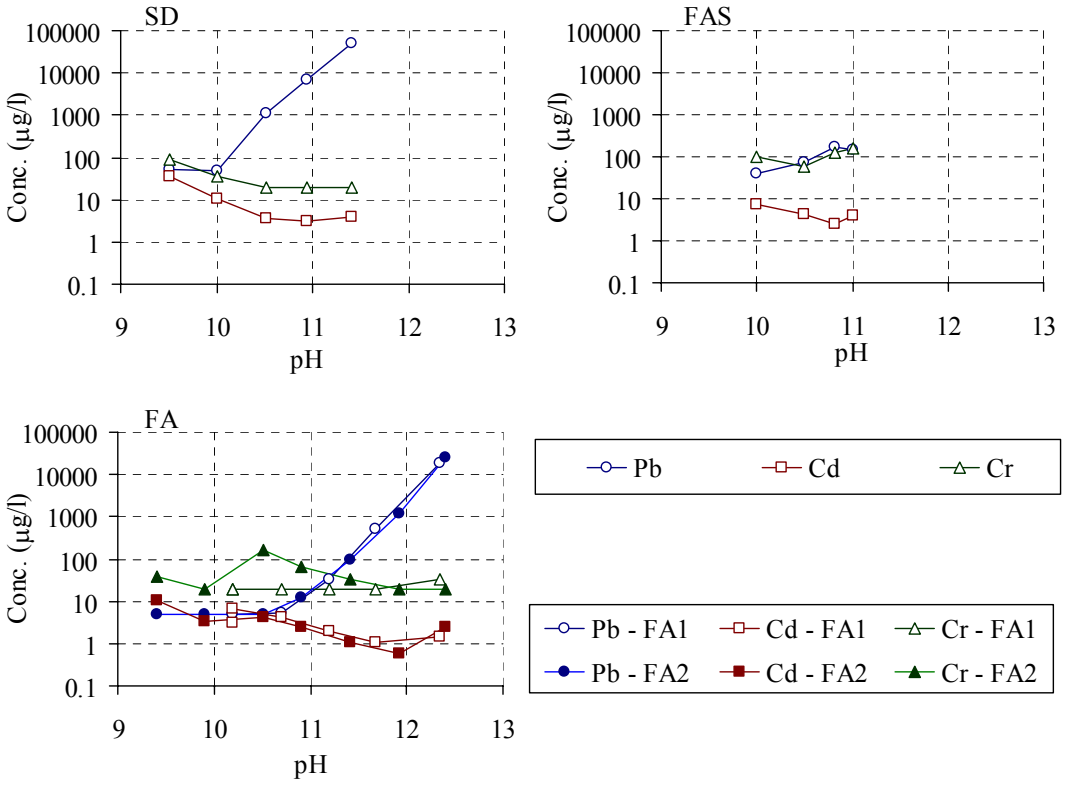

Figure 3.8. Concentrations of dissolved Pb, Cd, and Cr in the suspension as a function of pH during treatment of three types of residues from MSWI. pH was adjusted stepwise downwards with addition of H_2SO_4 (SD) or $FeSO_4$ (FA and FAS). SD is a semidry APC-residue, FA is a pure fly ash, and FAS is a fly ash mixed with sludge. The experiment was repeated on fly ash, hence FA1 and FA2.

The optimum pH is a balance as it controls the content of Cd, Cr, and Pb. If Pb is not considered a problem, a high pH is desired to ensure low concentrations of Cd and Cr. On the other hand, a pH below 10 will yield low Pb concentrations, but at the expense of an increase in the concentrations of Cd and Cr. It is possible to reduce the content of Pb in water substantially without increasing the concentrations of Cd and Cr to an unacceptable level. Table 3.2 shows the pH intervals for three pH-controlling chemicals and three types of residues based on results from [5] and [6], in which the concentrations of Cd, Cr, and Pb were below 10 μg/l, 100 μg/l, and 100 μg/l, respectively. In comparison, the recommended limits for discharge of wastewater to a public wastewater treatment plant in Denmark is Cd ≤ 3 μg/l, Cr ≤ 300 μg/l, and Pb ≤ 100 μg/l (Danish EPA, 1994).

Table 3.2. pH values with Pb being below 100 μg l^{-1}, Cd being below 10 μg l^{-1}, and Cr being below 100 μg l^{-1} in each experiment based on results from [5] and [6]. SD is a semidry APC-residue, FA is a fly ash and FAS is a fly ash mixed with sludge from a wet scrubber system. All pH values are without temperature compensation.

	CO_2	$FeSO_4$	H_2SO_4
SD 1	10.1-10.3	10.0-10.8	10.0-10.2
SD 2	10.3-10.5	9.4-10.5	
FA 1	NI[1)]	< 10.2-11.4	[2)]
FA 2	NI[1)]	9.4-11.4	
FAS	10.0-11.2	10.0-10.6	[2)]

[1)] No pH interval where the criteria are observed.

[2)] H_2SO_4 has not been used on fly ash and fly ash mixed with sludge.

The actual choice of agent for adjusting and maintaining pH depends on the actual circumstances. The costs will probably play an important role. For instance, if flue gas containing 5-10 % CO_2 is readily available this may be preferred even though it may yield slightly elevated concentrations of trace elements in the wastewater. If CO_2 is not available, $FeSO_4$ has the advantage of being used already in the Ferrox-process (during the mixing) and it is therefore available with a very limited additional investment for required equipment. When treating semidry or dry APC-residues a cheaper agent such as H_2SO_4 could be preferred because these residues have a high and very fluctuating content of readily available hydroxide that is not fully bound by the addition of iron(II) during the mixing. For these kinds of residues the amount of $FeSO_4$ added during mixing is high and therefore, the use of H_2SO_4 is considered safe also with respect to long-term stability.

3.6.2 Reaction time

The experiments, in which the pH level was changed stepwise with simultaneous measurements of the concentrations in the suspension, it was assumed that a near equilibrium state was reached for Cd, Cr, and Pb. In the experiments, which described the relationship between the wastewater concentrations and pH, constant pH was maintained for 10 minutes. A supplementary study has been made, in which the relationship between time and the concentrations in the wastewater at a constant pH is established. These experiments are described in detail in [5] and [6]. Figure 3.9 illustrates the concentrations of Cd, Cr, and Pb as a function of the time that pH was maintained constant during treatment of a semidry APC-residue are shown as an example (from [6]). From this study it appears that Cd reaches near equilibrium immediately and is therefore primarily dependent on pH. Pb needs time in the order of minutes to reach near equilibrium. The relation between the behaviour of Pb and pH is very consistent with data provided in literature (Chandler et al., 1997) from which it appears that Pb is primarily dependent on pH and secondary on the elapsed time. Cr is very slowly released and the change in the concentration of Cr in the wastewater during the study presented in [5] and [6], where pH was stepwise lowered, could instead of pH be a feature of the elapsed time. On the other hand a decrease in the Cr concentration with an increasing pH is consistent with data from Chandler et al (1997). Therefore the time that pH will have to be maintained should be limited and just long enough to ensure a low concentration of Pb so that an increasing release of Cr to the water is avoided.

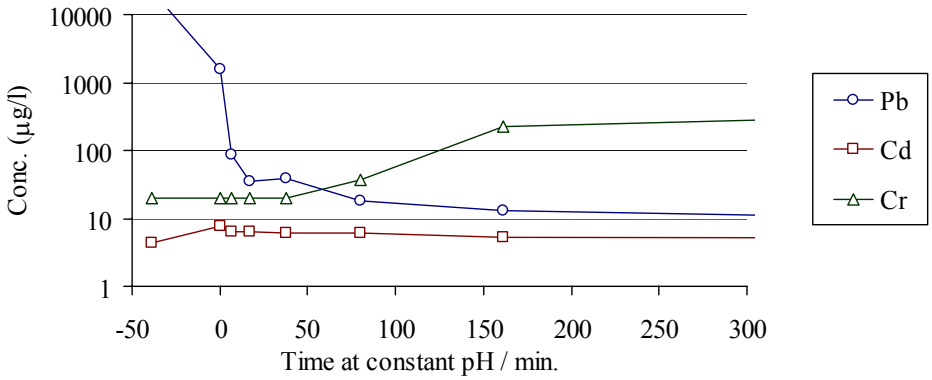

Figure 3.9. Concentrations of dissolved Pb, Cd, and Cr in the suspension as a function of the time pH was kept constant with the addition of small amounts of CO_2 during treatment of a semidry APC-residue (SD). pH was maintained constant at 10.45 from the time 0 minutes.

Table 3.3. pH and reaction time for Ferrox-treatment of semidry APC-residue, fly ash and fly ash mixed with sludge. SD is a semidry APC-residue, FA is a fly ash and FAS is a fly ash mixed with sludge from a wet scrubber system.

Residue treated	SD	FA	FAS
pH controlling agent	H_2SO_4	$FeSO_4$	$FeSO_4$
Recommended pH	10.4[1]	11.0	10.8
Reaction time[2]	60 minutes	30 minutes	30 minutes

[1] 10.3 if the temperature rises above 40 °C.

[2] From pH adjustment starts.

Based on experience gained in the studies described in [5], [6], and in some preliminary studies, the recommended pH and reaction time for Ferrox-treatment of semidry APC-residue, fly ash and fly ash mixed with sludge can be set up. These values are shown in Table 3.3. The listed values have been used for the stabilisation of a semidry APC-residue, a fly ash and a fly ash mixed with sludge in [4] and this resulted in wastewater with a low content of Cd, Cr, and Pb as shown in Table 3.4. Compared to the studies made in a laboratory scale in [1] and [3] where Cr concentrations up to 2500 µg/l were observed, the concentration of Cr is very low (up to 90 µg/l). This difference is probably due to the time control in the semi-industrial scale process because the aeration took 24 hours in the laboratory. Furthermore, the low concentrations of Pb can also be assigned to the adjustment and maintenance of a specific pH.

Table 3.4. Composition of the wastewater discharged from the Ferrox-process. SD is a semidry APC-residue, FA is a fly ash and FAS is a fly ash mixed with sludge from a wet scrubber system. The samples have been filtered through 0.45 µm polypropylene.

Residue treated	Unit	SD	FA	FAS
pH		10.4	10.9	10.8
Cd	µg/l	6.4	2.6	5.7
Cr	µg/l	68	90	4.0
Pb	µg/l	69	28	47

The amount of chemicals used for adjusting and maintaining pH depends on the desired pH and on the acid neutralisation capacity of the residues. Some experience with the amounts required for this has been obtained for a period, during which 19 batches of semidry APC-residue and 26 batches of fly ash were Ferrox-treated with the pH values from Table 3.3 at the plant described in [4]. On average 2.0 % (w/w residue) of H_2SO_4 and 0.45 % (w/w residue) of $FeSO_4$ was added in order to adjust and maintain pH during treatment of a semidry APC-residue and a fly ash, respectively. Prior to this 49 g

Fe per kg semidry APC-residue and 13 g Fe per kg fly ash had been added during the mixing with water and residue. In the study of the Ferrox-process in a semi-industrial scale (see [4]) 0.9 % (w/w residue) of H_2SO_4 and 0.7 % (w/w residue) of $FeSO_4$ was added in order to adjust and maintain pH during treatment of semidry APC-residue and fly ash, respectively. In the same study 0.1 % (w/w residue) of $FeSO_4$ was added in order to adjust and maintain pH during treatment of fly ash mixed with sludge.

3.7 Separation

The fourth step involves separating the solids (the Ferrox-product) from the water (the wastewater). At a plant similar to the one depicted in Figure 3.1, separation is done in a separate unit (in this case a plate-and-frame filter press). The separation takes place immediately after the pH has been adjusted and maintained for the desired time. The outcome of this process is the Ferrox-product and the wastewater. The latter will be discussed in this section, whereas the Ferrox-product, which is subsequently washed, is described in the next section. The possible separation equipment is not discussed here and is regarded as a specific technical discipline with a comprehensive literature, which can be consulted if desired. However, it can be said that a plate-and-frame filter press has been successfully used at the plant as described in [4]. This plate-and-frame filter press can be seen in Figure 3.7. Furthermore, vacuum band-pass filters are used routinely for dewatering suspensions containing APC-residues.

Full separation of the solids from the wastewater cannot be expected. Wastewater equal to typically L/S 1 l/kg is left in the solids after separation. Therefore, the amount of water leaving as wastewater from the process is typically given as the amount of water added to the process in the mixing minus the amount left in the solids. In the studies performed in [4] and [6] a dry matter content of 50-60 % was routinely achieved in the dewatered Ferrox-product. The amount of wastewater discharged from the Ferrox-process as described in [4] is shown in Table 3.5.

The composition of wastewater depends on the residue treated and on how the process is carried out, e.g. whether the pH has or has not been adjusted during the process. One of the objectives of the process is to keep the requirements to the wastewater treatment at a minimum. As the process also aims at removing easily soluble salts with the wastewater, a high content of these salts will have to be accepted. The pH of the wastewater is designed in the process so that high concentrations of trace elements are avoided and is, therefore, fixed. It is fairly easy to lower pH to an acceptable level, e.g. by aeration (Environment & Resources DTU et al., 1999). The content of trace metals is more critical due to the higher costs associated with the removal of such metals.

Table 3.5. Quantity and composition of the wastewater discharged from the Ferrox-process run on a semi-industrial scale plant [4]. SD is a semidry APC-residue, FA is a fly ash and FAS is a fly ash mixed with sludge from a wet scrubber system. The samples were filtered through 0.45 μm polypropylene.

Residue	treated Unit	SD	FA	FAS
Wastewater	m^3/tonne untreated residue	2.8	2.3	2.4
pH[1]		10.7	11.1	11.0
Cond.	mS/cm	140	91	72
Ca	mg/l	19 000	2000	1300
Cl	mg/l	52 000	28 000	21 000
Fe	mg/l	0.050	< 0.05	0.085
K	mg/l	7500	12 000	10 000
Mg	mg/l	1.8	< 0.9	< 1.4
Na	mg/l	7400	10 000	8400
S	mg/l	280	1100	1600
Al	μg/l	590	6100	36 000
As	μg/l	7.0	< 5	12
Ba	μg/l	3000	1400	420
Cd	μg/l	6.4	2.6	5.7
Co	μg/l	< 0.25	< 0.25	< 0.25
Cr	μg/l	68	90	4.0
Cu	μg/l	7.3	< 5	11
Hg	μg/l	0.32	1.0	0.25
Mn	μg/l	1.6	1.8	3.3
Mo	μg/l	720	1600	830
Ni	μg/l	< 2.5	< 2.5	< 2.5
Pb	μg/l	69	28	47
Zn	μg/l	120	24	45

[1] Including a temperature compensation on +0.3 unit for SD and +0.2 unit for FA and FAS.

Within certian limits, the content of trace metals can be designed during the adjustment of pH. However, this depends on which elements are regarded the most critical. Table 3.5 provides an example of a wastewater composition. The example is from the study described in [4] on the Ferrox-process in a semi-industrial scale. In this study Cd, Cr,

and Pb were considered the critical elements. The very high specific conductivity is typical of wastewater, especially of wastewater from treatment of semidry APC-residue. The latter caused by a high content of $CaCl_2$ in this type of residue. This can also be seen from the higher content of Ca and Cl in the wastewater from treatment of semidry APC-residue. If an anion/cation balance is set up, based on the values in Table 3.5 for Cl, S (as a divalent anion), Ca, K, and Na, the balance fits with 2.7 %, 2.3 %, and 0.0 % for the SD, FA, and FAS, respectively. Thereby, the result is verified. The dominating anion is chloride, which accounts for 86 - 98 % of the negatively charged equivalents. When treating semidry APC-residue the dominating cation is Ca, which accounts for one third of the positively charged equivalents. When treating fly ash and fly ash mixed with sludge, Na is the dominating cation accounting for approx. half of the positively charged equivalents. From the content of iron given in Table 3.5 it can be established that iron is precipitated as a result of the high pH and the oxidation. The content of Cd, Cr, and Pb is fairly low especially if the wastewater is regarded as the result of an extraction at L/S 3-4 l/kg and compared with the corresponding figures for leaching/extraction of untreated APC-residues in the literature (COWIconsult, 1995). However, the regulatory limits that have to be complied with in each case will serve as a yardstick for what is acceptable. Modelling of the content of trace elements is very difficult due to the high salinity of the water and because equilibrium cannot be assumed.

3.8 Washing

The final step in the Ferrox-process is the washing of the residues, upon which the APC-residue is considered stabilised as a Ferrox-product. The Ferrox-product is described separately in the next chapter. The washing procedure follows immediately after the separation and can conveniently take place in the same unit as the separation. At a plant similar to the one depicted in Figure 3.1 the final washing is carried out on the plate-and-frame filter press (see Figure 3.1). The water used for washing can be reused in the mixing as discussed earlier in this chapter.

The Ferrox-product has a water content of approx. 50 % after the separation depending on the technique used. The washing aims at replacing this water, which has a composition similar to that of the highly saline wastewater, with fresh water. Furthermore, some salts will dissolve during the washing and be removed with the water. This improves the removal of salts during the treatment. Figure 3.10 shows the relative amount of Cl and K removed with the wastewater and during washing. Figure 3.10 is based on data obtained during the study described in [4]. From Figure 3.10 the washing can clearly be seen to remove a substantial amount of both Cl and K equal to approximately 20 % of the total amounts of both Cl and K removed during the process. In [1] the composition of the wastewater (process water) and the washing water equal to L/S 1 l/kg is shown (Table 3). From this it appears that the composition is very similar

for these two water fractions, which indicates that the washing actually replaces the residual wastewater from the separation.

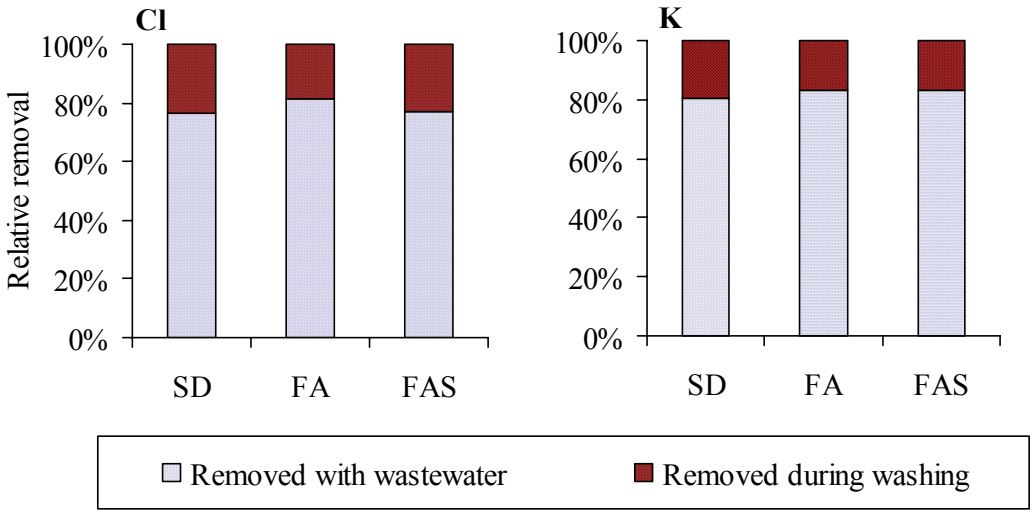

Figure 3.10. The relative removal of Cl and K with the wastewater and during the washing. 100 % equals the sum of either Cl or K removed with the wastewater and during the washing. SD is a semidry APC-residue, FA is a pure fly ash, and FAS is a fly ash mixed with sludge.

The progress of the washing can be measured by the specific conductivity in the out-let from the unit where the washing takes place. Using the specific conductivity is convenient and from the decreasing conductivity it can be detected when most of the easily soluble salts are removed and how the washing progresses. However, for a more detailed description of the washing this technique is not sufficient. Using the specific conductivity has been successfully used in the studies described in [4] and [6]. Figure 3.11 illustrates the conductivity in the out-let from the plate-and-frame filter press and the accumulated removal of Cl as a function of the amount of water washed through during washing of a Ferrox-treated semidry APC-residue can be seen. Figure 3.11 origins from [6] and illustrates the progression of the washing.

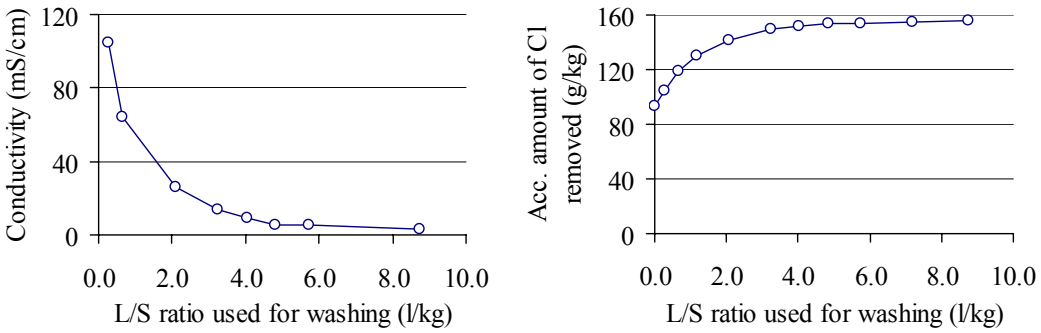

Figure 3.11. The conductivity in used water from washing and the accumulated amount of Cl removed during washing as a function of the amount of water washed through during washing of a Ferrox-treated semidry APC-residue.

If washing solely replaces the residual wastewater in the Ferrox-product there is no upper limit for the flow of water as the only action is a dilution. However, if salts are also dissolved then a better removal might be achieved if the flow of water through the Ferrox-product is slow. The ideal removal would require an infinitely slow flow. However, other considerations as to the flow of the washing water include the feasibility of the washing. If the washing is done in a technical scale it should be fast. This is required because the equipment used for separation/washing is a critical component with respect to the capacity of a plant for the Ferrox-process and to the costs. It should therefore be as small as possible. In a study presented in [6] the impact of the flow during the washing on the semi-industrial scale plant described in [4] is discussed. There is apparently no visible difference whether the flow in this case is L/S 3.5 l/kg per hour and L/S 12 l/kg per hour (figures derived from the study presented in [6]). This might suggest that the dilution of the residual wastewater in the Ferrox-process is the primary action. The limit for the flow of the washing water in a technical scale is therefore primarily governed by the equipment.

The water used for washing has to be fairly clean with respect to salts. In the end, the quality of the washing water sets the limits for how good a removal of salts that can be achieved. Therefore, the quality of the water used for washing primarily depends on the desired quality of the Ferrox-product. Similarly, the amount of water used for washing is governed by the desired quality of the Ferrox-product. The more water used, the more salts are removed. In the study performed in [4], with APC-residues being stabilised in a semi-industrial scale, the major part of the easily soluble salts, e.g. Cl and the easily soluble fractions of K and Na, were removed, whereas gypsum was not removed. In this study, the water used for washing was reused in the mixing process. The washing was done on a filter press, in which the Ferrox-product also had been dewatered. In the washing process, water equivalent to L/S 3 and 4 l/kg was used for washing Ferrox-products based on fly ash/fly ash mixed with sludge and semidry APC-residue, respectively. In [6] the required amount of water used in the washing (3-4 l/kg) is determined. Figure 3.11 provides an example of the progression of the washing for treatment of a semidry APC-residue. It appears that using 4 l/kg of water is adequate, as additional water only has a marginal effect.

The use of 3-4 l/kg of water for the washing resulted in a removal of Ca, Cl, K, Na, and S as shown in Table 3.6. Si is included in the table as a conservative element to illustrate the uncertainty of the method. The figures in Table 3.6 show that especially Cl, K, and Na are removed, whereas the content of S is virtually unchanged or increased due to the addition of ferrous sulphate. Ca is only partly removed during the treatment due to its presence in gypsum. The removal of K and Na is between 72 % and 87 %. The remaining K and Na might be bound in minerals with low solubility (Chandler et

al., 1997) and can therefore not be fully removed during the process. The latter is supported by Figure 3.2, which resample the amount of K removed during the process and amount leached subsequently by a batch test at L/S 10 l/kg. Figure 3.2 is based on the study presented in [4]. As it can be seen, most of the available K is removed during the process. The leachable amount equals 1-4 % of the total available amount (the sum of the removed and the leached K).

Table 3.6. Salt removal and weight reduction during the Ferrox-process. All figures are in % (w/w) removed during the process. SD is a semidry APC-residue, FA is a fly ash and FAS is a fly ash mixed with sludge from a wet scrubber system.

	SD	FA	FAS
Ca	31	15	7
Cl	99	98	92
K	87	81	79
Na	82	74	72
S	– 84	– 3	5
Si	3	2	– 1
Mass loss	14	7	7

The removal of salts with the wastewater and subsequently during washing results in an overall mass loss despite the addition of ferrous sulphate. The mass loss has been calculated in [1] to be 10 % or 21 % of the initial amount of residue treated for treatment of semidry APC-residue and fly ash, respectively. In [4] the mass loss is calculated on the content of a range of conservative elements in the untreated APC-residues and their corresponding Ferrox-products. The mass loss found in this way is shown in Table 3.6. Apparently the mass loss determined in [1] and [4] does not correspond. However, the method used in [4] is considered to be the most accurate and the mass loss shown in Table 3.6 is therefore a better indication of the expected mass loss of the APC-residues during the Ferrox-process. The figures are, however, only indicative as the mass loss depends on the composition of the APC-residues. The loss of weight is an advantage as regards the subsequent handling and disposal of the Ferrox-product.

4. FERROX-PRODUCT

This chapter provides an outline of the characteristics of the Ferrox-product. The aim of the Ferrox-process is to improve the leaching characteristics of the APC-residues. Therefore emphasis is placed on the leaching properties of the stabilised residues, i.e. the Ferrox-products.

4.1 Characterisation

The addition of iron, which is subsequently oxidised, changes the colour of the residue from grey to brownish/yellow/reddish. The moist Ferrox-product is thus similar to clay, also with regard to the consistency. Figure 4.1 shows a photo of a Ferrox-product as a filter cake on a plate-and-frame filter press. The photo was taken in the semi-industrial scale plant described in [4].

Figure 4.1. Ferrox-product on a plate-and-frame filter press from the semi-industrial scale plant described in [4].

In [1] and [4] the Ferrox-products have been characterised. In [4] the characterisation is based on a total digestion. Figure 4.2 shows the distribution of the analysed elements in anticipated minerals and originates from [4]. The Ferrox-process aims at removing the

salts and immobilising the trace elements. Therefore, the composition of the Ferrox-product compared to the corresponding untreated APC-residue is characterised by a substantially lower content of especially Cl, but also of K and Na. 90 – 99 % of the initial content of Cl is removed during the process. Furthermore, the addition of iron increases the content of iron. The content of sulphate is doubled when treating semidry APC-residue due to the large amount of sulphate that is added during treatment (as $FeSO_4$ and H_2SO_4). For fly ash and fly ash mixed with sludge, only minor increases in the content of S were observed. As salts are washed out during the treatment the trace elements are slightly concentrated in the Ferrox-product compared to the raw APC-residue. The result presented in Figure 4.2 represents one sampling of untreated residue and the corresponding Ferrox-product as described in [4]. During the entire period (14 months), in which the semi-industrial scale plant described in [4] was in operation, the raw APC-residues were sampled. After this period a combined sample for each type of APC-residue was made. This resulted in three samples (a semidry APC-residue, a fly ash and fly ash mixed with sludge), which, to some extent represent the average composition of the APC-residue from the respective MSWI. The composition of these samples where determined by total digestion in parallel to the analysis described in [4]. A comparison of the composition of the APC-residue used for the study presented in [4] and of the combined samples showed that there were only minor differences. Hence the APC-residues used in [4] are representative of the APC-residues from the respective MSWI.

The alkalinity or ANC (acid neutralisation capacity) of the Ferrox-product is an important issue in order to predict long-term stability. If a cation/anion balance is set up for the result of the characterisation presented in [4], a large proportion of Ca has to be bound in calcite or portlandite in order to even out the cation/anion balance as it appears from Figure 4.2. Table 4.1 shows the alkalinity bound in calcite and portlandite as described in [4]. It appears that the Ferrox-process decreases the alkalinity slightly when treating semidry APC-residue. This corresponds to the fact that treating semidry APC-residue requires more $FeSO_4$ and H_2SO_4 than fly ash. The slightly increased alkalinity of Ferrox-treated fly ash and fly ash mixed with sludge compared to the untreated residues can be partly ascribed to the concentration of those components in the solids that are not solubilised. In [1] the ANC of an untreated semidry APC-residue, an untreated fly ash and their corresponding Ferrox-products is determined by adding acid in excess and subsequently titrating back to pH 7. It is found that the ANC in the Ferrox-products is slightly reduced (5-12 %), but still has a high ANC of 6.9 – 7.5 eq/kg.

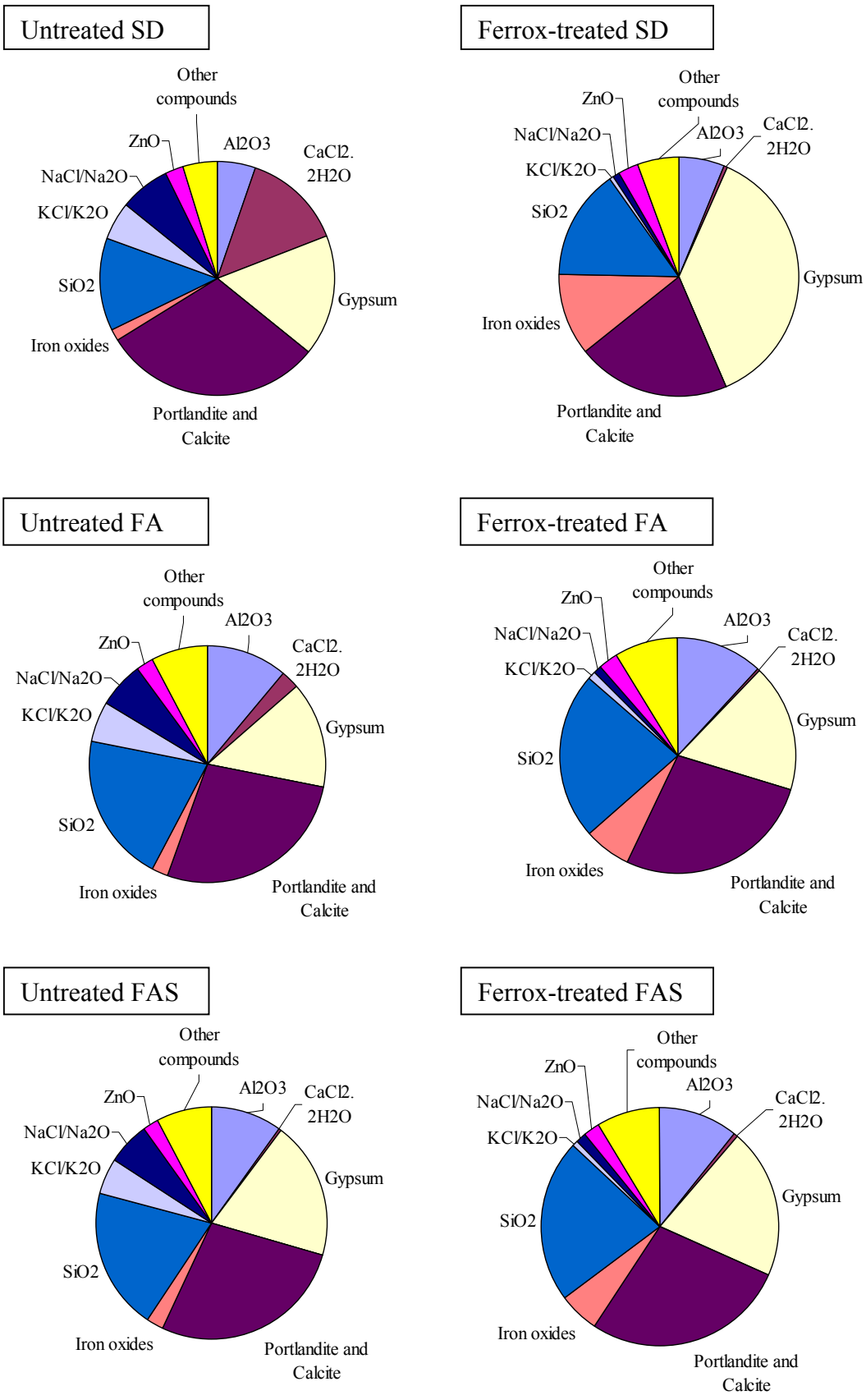

Figure 4.2. Anticipated mineralogical composition of untreated and treated residues based on the content of elements. SD is a semidry APC-residue, FA is a fly ash and FAS is a fly ash mixed with sludge from a wet scrubber system.

Table 4.1. The alkalinity as eq/kg bound in calcite and portlandite in untreated residues and Ferrox-products described in [4] in eq/kg. SD is a semidry APC-residue, FA is a fly ash and FAS is a fly ash mixed with sludge from a wet scrubber system.

Residue	SD	FA	FAS
Untreated	7.2	7.1	6.8
Ferrox-treated	6.1	7.7	7.8

The alkalinity of the Ferrox-products has been described in a study not yet published, however performed in parallel to the study described in Astrup et al. (2001). This study was based on the Ferrox-products described in [4] and used the analytical techniques described in Astrup et al. (2001). It was found that the alkalinity (determined by titration and extraction with acid until pH 4.5) was approx. 5 eq/kg and 4.5 eq/kg for Ferrox-products based on semidry APC-residue and fly ash, respectively. The similar figures for the untreated semidry APC-residue and fly ash are 7 eq/kg for both residues. As approx. 2 eq/kg alkalinity is bound by addition of $FeSO_4$ and H_2SO_4 when treating semidry APC-residue, the figures from the study performed by Astrup et al. of the alkalinity fit. The release of iron in a pH static leaching at pH 4 shows that alkalinity bound by the added iron is not released, (Environment & Resources DTU et al., 2001). The figures for untreated fly ash and the corresponding Ferrox-product (7 eq/kg and 4.5 eq/kg, respectively) do not fit as well because only 0.7 eq/kg alkalinity is bound during the process. However, the studies performed by Astrup et al. suggest that the Ferrox-products described in [4] have a fairly high alkalinity of more than 4 eq/kg. The alkalinity of fly ash mixed with sludge and the corresponding Ferrox-product has not been investigated, but in Hjelmar (1992) an alkalinity of 4.5 eq/kg is reported for a mixture of fly ash and wet scrubber sludge. As the wastewater is neutralised during treatment to a pH of approx. 9 before precipitating the sludge, the sludge is not expected to reduce the alkalinity of the fly ash when mixed. On the contrary Hjelmar et al. (1990) reports that sludge from the wet scrubber has a content of calcium carbonate and calcium hydroxide. Therefore, the ANC of fly ash mixed with sludge is expected to be equivalent to or higher than that of pure fly ash.

Overall, the Ferrox-process does not appear to alter the ANC or alkalinity substantially and in the studies performed in connection with this project the changes imposed by the addition of iron(II) on the Ca-buffer systems are less significant.

4.2 Leaching properties

The leaching properties of the Ferrox-product have been described in several studies ([1], [3], [4], and Environment & Resources et al. 1999). In all these studies the

leaching properties vary to a relatively low extent. This is described in the section about robustness. Therefore the following section - in which a comparison of the leaching properties of the treated and untreated residues are described - is primarily based on the results obtained in [4] because this study incorporates all the latest modifications to the Ferrox-process and thereby represents state-of-the-art for the Ferrox-process when applied on semidry APC-residue, fly ash, and fly ash mixed with sludge. Furthermore, this study represents the most comprehensive work done on Ferrox-products including a detailed documentation of the process.

4.2.1 Robustness

The relative robustness of the products with regard to changing process conditions can be evaluated by comparing the results of a batch leaching test (L/S 2 l/kg, 6 hours) for the Ferrox-products described in [1] and [4] as done in Table 4.2. These two studies have been conducted in a laboratory scale and a semi-industrial scale, respectively and with major differences in the added amount of iron(II), the time of aeration, addition of pH controlling agent, wash of the Ferrox-product, reuse of washing water, etc. The APC-residues used in these two studies were not from the same sampling. Table 4.2 illustrates that the concentrations in the leachate from the tests of the two Ferrox-products, in which the treatment has been modified in many ways, is in the same order of magnitude. The leaching of Cd and Pb is reduced substantially by the Ferrox-process and despite the different process conditions the leaching from the Ferrox-products are in the same order of magnitude which suggests a robust process with regard to changes in the process configuration.

Table 4.2. Comparison of the concentrations of selected elements in a batch compliance test (L/S 2 l/kg, 6 h.) of Ferrox-products described in [1] and [4]. SD is a semidry APC-residue and FA is a fly ash.

Residue treated		SD		FA	
		Source: [1]	Source: [4]	Source: [1]	Source: [4]
Cl	mg/l	8300	890	300	740
K	mg/l	1010	416	150	650
Cd	µg/l	0.84	< 0.52	1.1	< 0.41
Pb	µg/l	21	6.6	36	8.7

The robustness towards changes in the process configuration discussed above has been supported by various studies prior to or presented in [1] – [6], with substantial reductions in the leaching of Cd and Pb being obtained throughout the project regardless of the changes in the process configuration with the exception of the amount of iron added. If less than 1 % iron or 4 % iron is added during treatment of a pure fly ash or a semidry residue, respectively, then an increased release of Cd and Pb can be observed [2].

4.2.2 Leaching from untreated and Ferrox-treated APC-residues

Leachability of Pb

Pb is one of the most important pollutants from APC-residues from MSWI because these residues often yield a high pH in the leachate, which mobilises the amphoteric Pb. The leachate can contain up to and above 1 g/l of Pb (Chandler et al., 1997; Hjelmar, 1992). In the studies performed in [3] concentrations up to 4.3 g/l and 1.6 g/l were obtained in leachate from untreated semidry APC-residue and fly ash, respectively. Pb is therefore the primary element that the Ferrox-process aims at immobilising.

Figure 4.3 shows the result of a two stage batch leaching test, a column test and an availability test for three APC-residues: APC-residue, fly ash, and fly ash mixed with sludge together with the corresponding Ferrox-products done in the study described in [4]. As can be seen the release of Pb from the Ferrox-treated residues under realistic conditions (the column test) is low which corresponds to findings in all studies of the leaching properties of the Ferrox-products. The concentrations did not exceed 5 μg/l and were generally lower (< 2μg/l) even at low L/S ratios. A pH static leaching as the one performed in [1] and [4] and shown in Figure 4.4 (from [4]) reveals that the release of Pb from pH approx. 6 and up is below 1 mg/kg for Ferrox-stabilised semidry APC-residue and fly ash. The release of Pb from Ferrox-stabilised fly ash mixed with sludge is below 1 mg/kg from pH 7.8 and up. An explanation for this could be that treatment of fly ash mixed with sludge uses the least iron.

A comparison of the untreated residue and the Ferrox-stabilised residues shows that the Ferrox-process reduces the release of Pb 250-1000 times. In the batch test, which cannot be interpreted as realistic conditions but serves as a compliance test, reductions up to 36,000 times were observed. Due to the pH dependency of Pb during leaching, the reductions will probably vary with the pH of the raw residue and the relative reductions are therefore of limited value.

The availability of Pb from the Ferrox-products are generally much higher than what has been found to be leached in other leaching tests e.g. batch leaching test and column test (see Figure 4.3). In [4] it is argued that the low release of iron during the availability test and the relatively high release of Pb indicates that Pb is associated with the surface of iron. However, the possibility exists that another phase created during the Ferrox-process could play a role.

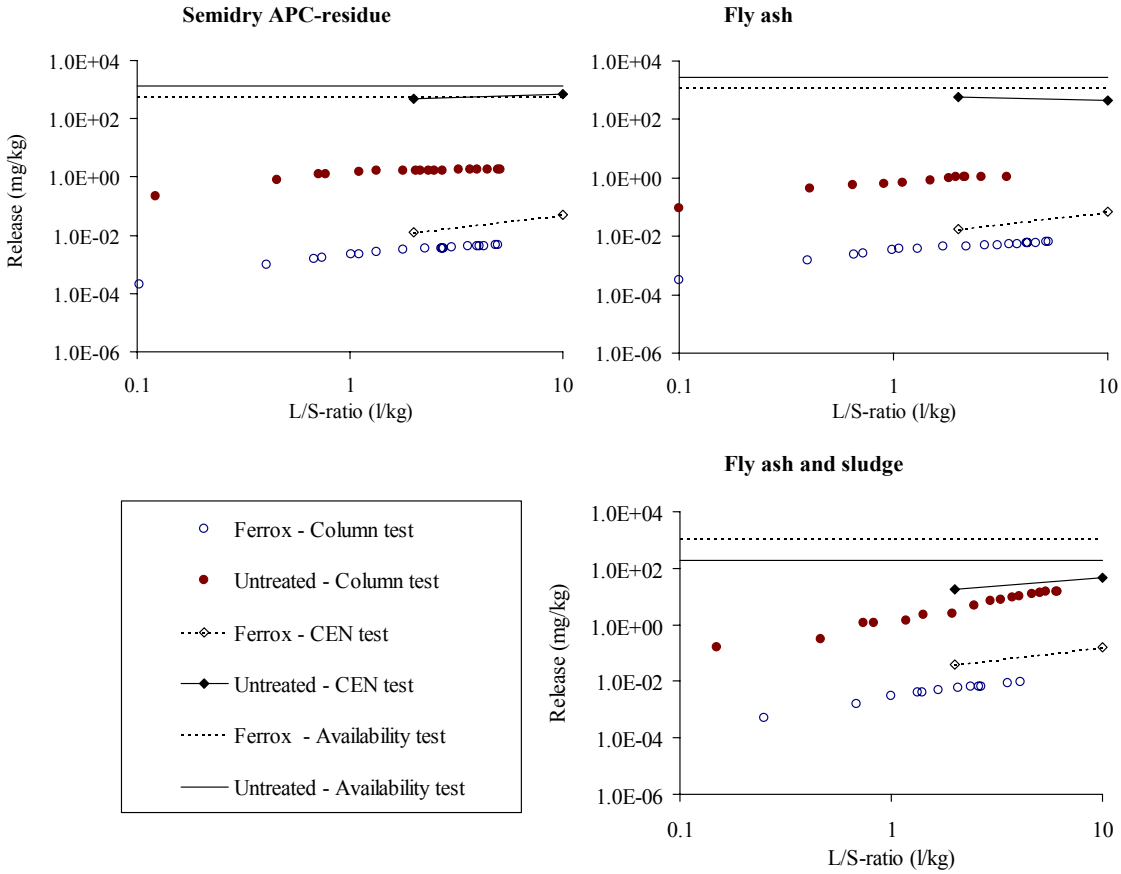

Figure 4.3. Release of Pb from treated and untreated residues during a two-stage batch-leaching test (CEN-test, L/S 2 and 10 l/kg), column test, and availability test. SD is a semidry APC-residue, FA is a fly ash and FAS is a fly ash mixed with sludge from a wet scrubber system.

The leaching results imply that the leaching of Pb from Ferrox-products on the short term is anticipated to be low. Hence, if the Ferrox-process is applied in full-scale no countermeasures are anticipated to be necessary to avoid an initial elevated concentration of Pb in the leachate. The release of Pb from the Ferrox-product on a long term basis is primarily governed by pH based on the result of the pH static tests and the knowledge of the leaching behaviour of the raw APC-residues (Chandler et al., 1997; Johnson, 2000; van der Sloot et al., 1997). Hence, the buffer systems are important. In this project, pH values below 8 are not reported from leaching tests in which pH is controlled by the solids. This indicates that the carbonate systems have not been depleted during leaching to L/S 10, which could equal leaching for hundreds of years depending on the disposal scenario (see [3]). It is therefore an indication that the Ferrox-product is able to withstand leaching for at least the same period. In Chandler et al. (1997) a comparison of small scale and large-scale laboratory column tests is made. The release in a large scale is only to be one fourth of that of a small-scale column test. In conclusion the release of Pb on a long-term basis is anticipated to be low.

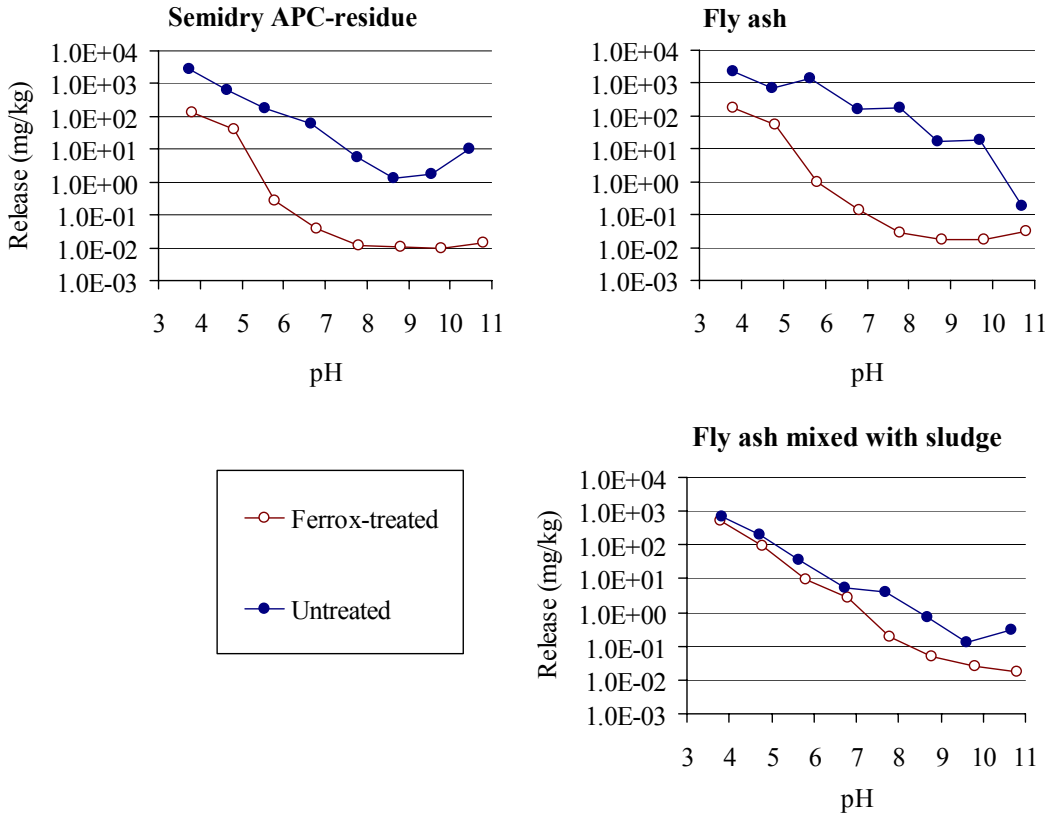

Figure 4.4. Release of Pb as a function of pH. Result of pH static leaching test (single batch, L/S 10 l/kg, 24 hours, and fixed pH) on Ferrox-treated and untreated residues. SD is a semidry APC-residue, FA is a fly ash and FAS is a fly ash mixed with sludge from a wet scrubber system.

Leachability of other trace elements

Besides Pb other trace metals are potential hazards to the environment when handling or disposing of APC-residues. These include As, Cd, Cr, Cu, Hg, Mo, Ni, and Zn.

Table 4.3 illustrates the release during a two-stage batch leaching test for untreated and treated residues. The figures in Table 4.3 are drawn from [4].

From the studies described in [1] and [4] the leaching of Cd, Cu, and Zn is found to be substantially reduced by treating the APC-residues with the Ferrox-process. In Table 4.3 an example of this can be seen. pH static leaching and column tests support this trend. A comparison of the results achieved in [1] and [4] reveal that the leachability of Cd, Cu, and Zn is slightly lower from the Ferrox-product described in [4] compared to the one described in [1]. The reason for this could be a slightly different pH (it is slightly higher in the test performed in [4]), changes in the used APC-residues and changes in the process configuration.

Table 4.3. Result of a two-stage batch-leaching test (CEN-test, L/S 2 and 10 l/kg) as accumulated release at L/S 10 l/kg. SD is a semidry APC-residue, FA is a fly ash and FAS is a fly ash mixed with sludge from a wet scrubber system.

Residue		SD		FA		FAS	
		Untreated	Ferrox	Untreated	Ferrox	Untreated	Ferrox
pH		12.52	11.29	12.69	11.23	12.05	11.17
As	mg/kg	0.063	0.054	0.074	0.032	0.084	0.082
Cd	mg/kg	0.012	< 0.002	0.13	< 0.002	0.032	0.0065
Cr	mg/kg	0.10	3.7	2.8	9.5	3.7	1.1
Cu	mg/kg	3.7	< 0.01	0.32	< 0.01	0.25	0.023
Fe	mg/kg	< 0.2	< 0.1	< 0.1	< 0.5	< 0.4	0.5
Hg	mg/kg	0.013	0.0024	0.0089	0.0009	0.017	0.0046
Mo	mg/kg	2.6	2.6	3.0	2.4	3.6	1.9
Pb	mg/kg	730	0.048	450	0.068	48	0.17
Zn	mg/kg	67	0.18	29	0.091	27	0.19

In addition to Pb, Cd, Cr, and Cl, the leachate from the column leaching test described in [4] was also analysed for a range of other metals. During the leaching test, concentrations in the leachate from Ferrox-products were below 10 μg/l for Ni. For Cu and Zn, the concentrations were below 6 and 79 μg/l, respectively. This suggests a low leachability of these elements from Ferrox-products.

The release of many of these elements is generally sensitive towards changes in pH, especially Cd and Zn (Chandler et al., 1997; van der Sloot et al., 1997). In this project a pH dependency during leaching from the Ferrox-products was observed for Cd, Cr, Cu, and Zn in [1] and [4]. Furthermore, the result of the pH static leaching test indicates that the release of Cd, Cu, and Zn was lower from the Ferrox-products compared to the corresponding APC-residues over a broad range of pH. In [3] a study is described where pH was between 8.35 and 9.0 during a leaching of a Ferrox-product based on a semidry APC-residue, similar to the Ferrox-product described in [1], but handled in a manner that allowed carbonation to take place. Leachate from this study with its relatively low pH contained less than 1 μg Cd per l, indicating that under realistic conditions, the release is lower than that found in the pH static test on the same Ferrox-product (see [1]). In the column test performed in [4], the concentrations of Cd in the collected leachate from Ferrox-products were below the detection limit (0.05 μg/l). In Chandler et al. (1997) a comparison of a small scale and a large-scale laboratory column test is made. The release in large scale is generally less than that of a small-scale column test. All this indicates that the release of Cd is low from the Ferrox-product over a wide pH range.

Another study (Astrup et al., 2001) describes the long-term development of pH in landfills with APC-residues. This work is based on the same residues as those used for the study performed in [4] and it appears that the pH of the leachate of a 10 m high deposit will remain above 8 for more than 50000 years even for a carbonated residue. The study is based on the assumption that the solubilities of mineral phases are the depleting factor. A parallel study has been made on the Ferrox-products described in [4] using the same analytical techniques. This study has not yet been reported but revealed that pH of the Ferrox-products would remain above 8 for leaching at an L/S-ratio of 2000-3000 l/kg corresponding to a time scale of 100,000 years for a 10 m high deposit.

The leaching results imply that the leaching of Cd, Cu, Pb and Zn is anticipated to be low in the short term. Hence, if the Ferrox-process is applied in full-scale, no countermeasures are deemed necessary to avoid an initially elevated concentration with regard to these elements. On a long-term basis, the release of Cd, Cu, and Zn are anticipated to remain low for an extensive period because the Ferrox-product buffers pH to an adequate level.

As for Pb, Cd is apparently associated with the surface of iron as argued in [4]. The availability of Cu and Zn from the Ferrox-products described in [4] were 310-490 mg/kg and 9000-10700 mg/kg, respectively. Hence, the availability of Cu and Zn compared to the release shown in Table 4.3 is much higher. Therefore, in parallel to Pb and Cd in [4], a comparison with the relatively low release of iron during the availability test suggests that Cu and Zn is also associated with the surface of the iron.

Based on the figures in Table 4.3 it seems that the Ferrox-process reduces the release of Hg. However, this does not concur with the results achieved in [1] and [3]. Predicting the impact of the Ferrox-process on the leachability of Hg is therefore difficult.

As, Cr, and Mo form oxyanions, which might prevent an effective immobilisation by surface complexation to the iron oxides (Stumm og Morgan, 1996). For As and Mo indications of a positive effect on the leachability was found in both a batch-leaching test (see Table 4.3) and in a pH static test performed in connection with the study presented in [4]. The result of the pH static test for As and Mo is shown in Environment & Resources DTU et al. (2001). The apparently higher release of Cr in the batch-leaching test from the treated residue (see Table 4.3) could be a feature of the design of the leaching test. When the untreated residue is brought into contact with water in a closed environment, reducing conditions may be formed and hereby Cr(VI) is reduced to the almost non leachable Cr(III). In the column test performed in [4], gas was generated in the column with untreated fly ash. This gas was analysed and consisted of hydrogen. This is a common feature of the untreated residues and described in Oberste-Padtberg and Schweden (1990). The leaching of Cr from the column with gas generation was very low, which suggests that a closed environment could affect the

leachability of Cr. Another explanation of the higher leachability of Cr from the Ferrox-product compared to the corresponding raw residue is that Cr(III) is partly oxidised during the stabilisation process and thereby mobilised as Cr(VI). This is, to some extent, supported by the observations made in [5] and [6] where Cr is found to be mobilised with time. In general, the results of the studies presented in [1]-[6] show no general trend with regard to the leachability of Cr.

Leachability of salts

APC-residues generally have a high content of salts e.g. $CaCl_2$, NaCl, and KCl. These are easily released when the residue is brought into contact with water. The result is a leachate, which poses a threat to the environment due to the high concentrations of salts. In this project concentrations in the range 100-400 g Cl per l has been observed in the initial leachate during column leaching from untreated APC-residues [3] and [4]. Many of the salts are rapidly depleted with increasing L/S-ratio giving a fast decrease in the leachate concentrations ([3] and [4]). In order to avoid this initial high release of salts, they are removed during the Ferrox-process, whereby the availability and leaching of salts as described in [4] are reduced. The removal of salt is anticipated to be partially dependent on the equipment and the method used for washing the Ferrox-product. As this has been subjected to on-going development, the discussion of the leachability of salts is primarily based on the study in a semi-industrial scale described in [4].

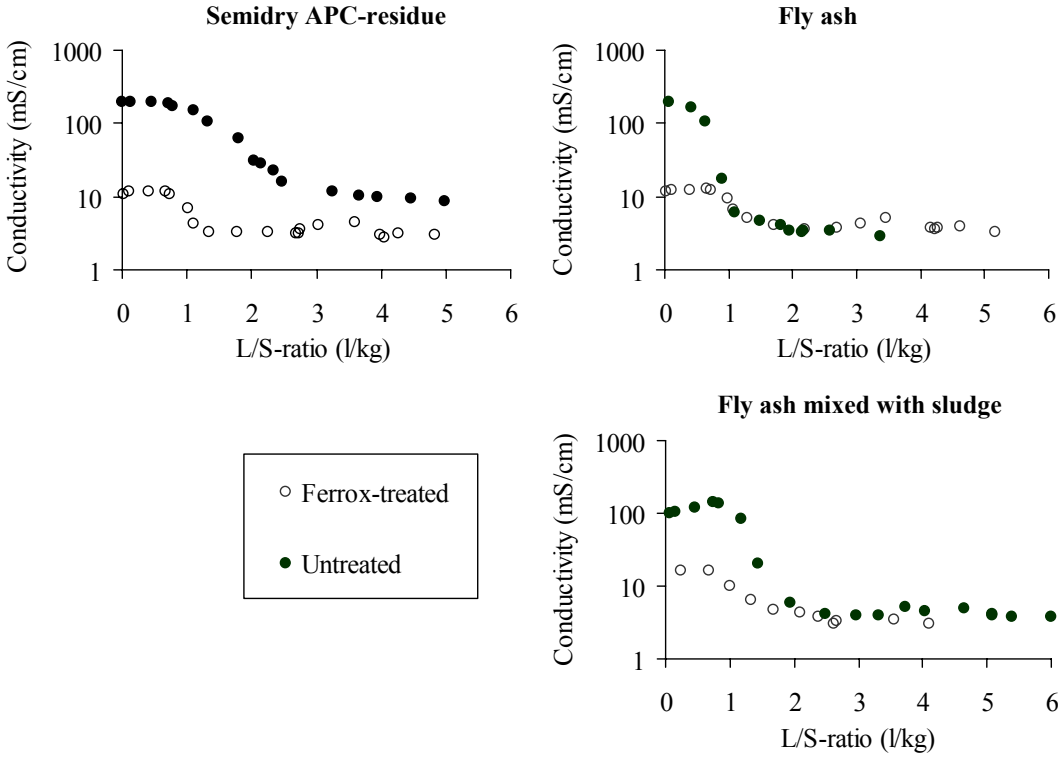

Figure 4.5. The specific conductivity as a function of the L/S ratio during a column leaching test described in [4]. SD is a semidry APC-residue, FA is a fly ash and FAS is a fly ash mixed with sludge from a wet scrubber system.

Figure 4.5 illustrates the specific conductivity as a function of the L/S-ratio during the column test described in [4]. As can be seen, the specific conductivity in the leachate from the Ferrox-product is much lower initially compared to that of raw APC-residue. At higher L/S ratios the specific conductivity in the leachate from the Ferrox-products remains on the same level or only slightly lower than the leachate from the untreated residues. This shows that the extraction of salts during the Ferrox-process is primarily beneficial with respect to short term leaching of salts as the initial release of large amounts of Cl, K, and Na is substantially reduced. Despite this, slightly elevated concentrations can be expected in leachate from Ferrox-products on a short-term basis. This is emphasised in Table 4.4, which provides a comparison of the concentrations of salts in the initial leachate from raw APC-residue and Ferrox-product. Furthermore, it appears that primarily Cl, K, and Na are removed, as it is discussed further in [4]. The leaching of salts from the Ferrox-product on a long-term basis is dominated by the content of Ca and sulphate, as can be seen from table 4.5 in [4]. Sulphate is added during the process where it precipitates with Ca to form a reservoir of solid gypsum in the Ferrox-product.

Table 4.4. The content of salts in the initial leachate during a column test performed in the study described in [4]. SD is a semidry APC-residue, FA is a fly ash and FAS is a fly ash mixed with sludge from a wet scrubber system.

Residue		SD		FA		FAS	
		Untreated	Ferrox	Untreated	Ferrox	Untreated	Ferrox
L/S-ratio	l/kg	0.12	0.021	0.061	0.020	0.15	0.25
Spec. Cond.	mSi/cm	200	10.9	195	12.0	103	16.6
Ca	mg/l	678	634	279	401	174	124
Cl	mg/l	252000	2517	106000	1645	38000	4916
Fe	mg/l	12[1)]	0.060[2)]	< 0.12	0.013[3)]	< 0.3[4)]	0.012
K	mg/l	5200	622	95000	783	3300	907
Na	mg/l	43335	1399	45000	1729	12000	1722
S	mg/l	58[1)]	828[2)]	1600	1260[3)]	4800[4)]	627

[1)] at L/S 0.45 l/kg
[2)] at L/S 0.41 l/kg
[3)] at L/S 0.40 l/kg
[4)] at L/S 0.47 l/kg

The concentration of salts in the leachate on a long-term basis is anticipated to be governed by the solubility of gypsum. However, the content of S present in Ferrox-treated fly ash and fly ash mixed with sludge remains at the same level as in the corresponding untreated fly ash and fly ash mixed with sludge, whereas the content in Ferrox-treated semidry APC-residue is approx. twice that of the untreated semidry APC-residue as discussed in [4]. Based solely on the solubility of gypsum, S will be

depleted after leaching to L/S 70-150 l/kg, which equals thousands of years' leaching in a realistic scenario (see [3]). The change imposed by the Ferrox-process on the gypsum content is therefore of minor importance with respect to leaching properties.

Leachability of iron

Iron oxides immobilise the trace elements in the Ferrox-product. Therefore, depletion of the iron could lead to an increase in the release of trace elements. The stability of the iron oxides has not been adressed directly here as it lay beyond the scope of this project. However, indirectly it has been adressed by examining the leaching of trace elements. During the leaching studies, the release of iron was observed and the results are briefly discussed below.

The release of iron from the Ferrox-product is very low also compared to the release of iron from the untreated APC-residues. The release of iron shown in Table 4.3 from Ferrox-treated fly ash mixed with sludge can be related to the iron added during the treatment as a worst case scenario as treatment of fly ash mixed with sludge requires the least iron(II) (13 g Fe/kg residue) and contains sulphite. The comparison shows that the added iron would be depleted after leaching to L/S 260 000 l/kg which equals millions of years. The actual circumstance for disposal of the Ferrox-product is, however, important as strongly reducing and acidic conditions potentially can dissolve the iron oxides and thereby release the trace elements associated with them.

5. CONCLUSION

The aim of this project was to develop the Ferrox-process towards a full-scale application with focus on the process parameters and their influence on the quality of the wastewater and the leaching properties of the stabilised APC-residues (the Ferrox-products).

A step by step examination of the Ferrox-process in the context of a full-scale application revealed the following process parameters to be the most significant:

- Amount of iron(II) added
  The amount of iron(II) added should exceed 30 kg/tonne and 5 kg/tonne for treating semidry APC-residue and fly ash, respectively. Table 5.1 shows the recommended addition of iron(II) for treating semidry APC-residue, fly ash, and fly ash mixed with sludge. The values given in Table 5.1 yielded a satisfactory result both with regard to wastewater and the leaching properties of the treated products.
- pH
  The pH during the process was found to be an important factor controlling the trace elements in the wastewater. A high pH favours a low content of Cd and maybe also Cr, but at the expense of a higher content of Pb in the wastewater. A low pH has the opposite effect, i.e. it yields a low content of Pb, but increases the content of Cd and Cr. It is documented that the pH can be controlled by CO_2, $FeSO_4$, or H_2SO_4 with good results. A set of recommended pH values is given in Table 5.1 for Ferrox-treatment of three types of APC-residues with either $FeSO_4$ or H_2SO_4 as the pH adjusting agent.
- Reaction time
  The time that pH is kept constant during the treatment before separation of the wastewater is important for the wastewater content of trace metals. The study establishes that a minimum time in the order of minutes will ensure a low concentration of Pb in the wastewater. Furthermore, a relatively short reaction time (in the order of minutes) is beneficial for avoiding elevated concentrations of Cr in the wastewater. A set of recommended reaction times are given in Table 5.1 for Ferrox-treatment of three types of APC-residues with either $FeSO_4$ or H_2SO_4 as the pH adjusting agent.
- Amount of water used for washing
  After separation of the wastewater, the majority of the remaining salts can be removed by washing the Ferrox-treated residues. Washing with water between L/S 3 l/kg or L/S 4 l/kg depending on the type of residue treated is found to be appropriate as recommended in Table 5.1. Washing at a higher L/S-ratio has only limited benefits for the leaching of salts from the Ferrox product, since the leaching is subsequently diffusion-controlled or solubility-controlled.

Equally important are the following process parameters that were found to be of minor importance, thus allowing some degrees of freedom in the choice of process configuration. These parameters comprise:

- Flow of washing water
  The washwater flow through the residual product seems to be of no consequence and may therefore be chosen freely, taking into consideration other factors, such as time.
- The quality of the water used for mixing
  The requirements for the quality of the water used for mixing are moderate, following which it is possible to reuse the water that has been used for washing the Ferrox-product. Reusing the water from washing for mixing had apparently no impact on the removal of salts from the residues treated. Alternatively, brackish water could also be used.

From a technical point of view the most significant findings are:

- The Ferrox-process is able to cope with variations in the properties of the treated APC-residues based on experience gained so far. However, a very low content of readily available hydroxide could require the addition of base.
- The addition of ferrous sulphate can be controlled with good accuracy by an on-line measurement of the density and correlating it to the concentration of iron(II) on a weight-to-weight basis.
- Oxidation of the added iron(II) can be almost completed within 20-50 minutes in a large scale by use of atmospheric air.
- Determining the content of iron(II) in a suspension of APC-residue can be done after extraction with $HClO_4$, if the iron(II) is not bound in a crystalline matrix.

Table 5.1. A set of recommended process parameters for stabilisation of three types of APC-residues with the Ferrox-process. SD is a semidry APC-residue, FA is a fly ash and FAS is a fly ash mixed with sludge from a wet scrubber system.

APC-residue treated	SD	FA	FAS
Fe amount[1)]	4.9 % (w/w)	1.25 % (w/w)	1.25 % (w/w)
Aeration time	50 minutes	20 minutes	20 minutes
pH controller	sulphuric acid	ferrous sulphate	ferrous sulphate
Optimum pH	10.4[2)]	11.0	10.8
Reaction time[3)]	60 minutes	30 minutes	30 minutes
Washing L/S	4 l/kg	3 l/kg	3 l/kg

[1)] The amount added during the mixing in the beginning of the process.

[2)] 10.3 if the temperature is above 40 °C.

[3)] Measured from the beginning of the pH adjustment.

Based on the findings of this project a set of process parameters shown in Table 5.1 has been identified, which could serve as a base for the design of a full-scale plant for the Ferrox-process. This set of parameters should ensure a low content of trace elements

especially Pb, Cd, and Cr in the wastewater and good leaching properties of the stabilised residue.

The recommended process parameters have been used for documenting the quality of the wastewater and the leaching properties of the Ferrox-product in a semi-industrial scale, thereby indicating the expectations to a full-scale Ferrox-process. To give an impression of the use of resources, Table 5.2 sums up the resources needed during the Ferrox-process using the parameters in a semi-industrial scale including water added with the iron(II) solution. Furthermore, the amount of wastewater generated is included whereas energy consumption is not.

Table 5.2. The use of water and chemicals during the Ferrox-treatment. SD is a Semidry APC-residue, FA is a fly ash and FAS is fly ash mixed with sludge from a wet scrubber system.

		SD	FA	FAS
Water	m^3/tonnes untreated residue	3.9	2.7	3.2 [1)]
$FeSO_4 \times 7H_2O$	kg Fe/tonnes untreated residue	49	20	13
H_2SO_4	kg/tonnes untreated residue	9	0 [2)]	0 [2)]
Wastewater	m^3/tonnes untreated residue	2.8	2.3	2.4

[1)] The water which is a part of the added fly ash with the sludge, is not included.
[2)] H_2SO_4 is not used for treatment of FA and FAS.

The levels of trace elements in the wastewater from the Ferrox-process in a full-scale use can partly be controlled by the process parameters especially by the pH adjustment and the reaction time. An example of the concentration levels that can be expected for some selected elements using the recommended process parameters from Table 5.1 of a semi-industrial scale plant is given in Table 5.3.

Table 5.3. Expected concentration levels in wastewater using the recommended process parameters from Table 5.1 in full-scale.

	Unit	Conc. level
pH		10-11
Cond.	mS/cm	High
Cd	µg/l	1-10
Cr	µg/l	1-100
Pb	µg/l	10-100

Table 5.4. Expected concentration levels for selected elements in leachate from Ferrox-products on a short as well as a long-term basis.

	Unit	Conc. level
Cd	µg/l	< 1
Cu	µg/l	< 10
Pb	µg/l	< 10
Zn	µg/l	< 100

During the Ferrox-process, salts are removed from the APC-residues resulting in a low content of especially Cl but also of K and Na in the Ferrox-product. For Cl, more than 90 % is removed from the residue during the Ferrox-process. The Ferrox-products studied in this project all had high alkalinity, which was comparable to the alkalinity of the APC-residues.

The leaching properties of the stabilised APC-residues are generally very robust towards changes in the process configuration and the process parameters with the exception of the limitations on the amount of iron(II) added. Furthermore, the leaching properties seem to be independent of scale based on the performed studies in both a laboratory and a semi-industrial scale.

Comprehensive tests of the stabilised residual products compared with similarly untreated residual products show unequivocally that the leaching properties are significantly improved with lower leaching of Pb, in particular, as well as Ba, Cd, Cu, and Zn. Especially Pb will be leached in large quantities without preceding stabilisation. Based on the findings of this project, the release of Pb from the Ferrox-product is anticipated to be very low on both a short and a long-term basis. The release of other cation forming trace elements is in general also expected to be low. This includes Cd, Cu, and Zn. Table 5.4 displays some expected concentration levels in the leachate from Ferrox-products on a short as well as a long-term basis. Leaching of Hg and Ni is either unaffected or not uniformly affected by the process, but is generally low. The release of oxyanion forming elements is not anticipated to be lower than that of the untreated APC-residues. In several instances, leaching of Cr is higher from stabilised products, compared to the untreated residues. For Cr the redox conditions are important. The release of salts e.g. Cl, K, and Na is substantially reduced. The tests of leaching properties cover, among others, column leaching, CEN tests and pH-static leaching.

The performed step by step examination of the Ferrox-process in the context of a full-scale application including a study of the Ferrox-process in a semi-industrial scale did not reveal any major difficulties. However, this project has identified a number of scale dependent factors while developing the process from a laboratory scale to a semi-industrial scale, and other scale dependent factors might appear as the process is developed further into full-scale. It has proven possible to develop the Ferrox-process from a laboratory scale to a semi-industrial scale, which to a large extent uses the same techniques and equipment as a potential full-scale Ferrox-treatment plant. Overall, it seems feasible to use the Ferrox-process in full-scale as a batch process without compromising the quality of the wastewater and the stability of the Ferrox-product as it has been described up until now. Furthermore, a number of process parameters has been optimised for use in the design of a full-scale plant for the Ferrox-process. There are, however, a number of issues that need to be addressed further before putting the process into full-scale use as discussed in the chapter on recommendations for the future work.

6. FULL-SCALE PERSPECTIVES

Applying the Ferrox-process in a full-scale perspective depends partly on the technology as described in previous chapters, but also on the organisational and legislative framework into which these technology has to fit. As a result, the actual scenario, in which the Ferrox-technology should be put into practise, is difficult to predict. Other circumstances than purely technical and/or environmental issues could therefore play an important role and result in different overall process configurations for the Ferrox-process. As examples of full-scale application of the process, this chapter provides a description of three plants for the Ferrox-process based on three possible process configurations. The three examples are based on the work presented in this PhD thesis. The three basic configurations are:

1. A batch process,
2. A continuous process, and
3. An on-site treatment and landfilling process.

Each plant is designed to treat 10 000 tonnes of pure fly ash per year, but the examples could have been made with other combinations of capacity and type of APC-residue.

6.1 Batch run Ferrox-treatment plant

The first example is based on the technology described in [4] where the Ferrox-process is studied in a semi-industrial scale plant that is run batch-wise. The technology is shown in Figure 6.1. A plant for batch-wise stabilisation of APC-residues can be located at the MSW incinerator or adjacent to the landfill. It may be run on a 24-hour basis or during the daytime only. The plant is designed for stabilisation of APC-residues in batches each of 3.8 tonnes. Compared to the plant described in [4] the oxidation and pH-adjustment at the plant shown in Figure 6.1 is suggested to take place in separate units. This is done to reduce the residence time in the oxidation tank of each batch, which is energy consuming. In addition to these two units, the plant consists of a mixing tank and a separation/washing unit. In the first unit, iron(II), water, and APC-residue is mixed prior to oxidation and pH adjustment. In the separation/washing unit the wastewater is removed and the Ferrox-product is washed. The water from the washing step is reused for the mixing.

The plant is designed to run during normal working hours (1750 hours/year). The units are in use simultaneously, e.g. while one batch is transferred to the reaction vessel, another batch is mixed and awaits transfer to the oxidation vessel. This is done to increase plant efficiency and to reduce the size of the units. The size of each unit is determined by the batch size and is therefore relatively large. In the plant layout, the volume of each unit is added 20 % for stirring (The stirring increases the volume needed because of cavitation) and an additional 20 % for unforeseen capacity expansion. The

volume of the oxidation unit is added 50 % for dispersion of air in addition to the 20 % for unforeseen capacity expansion.

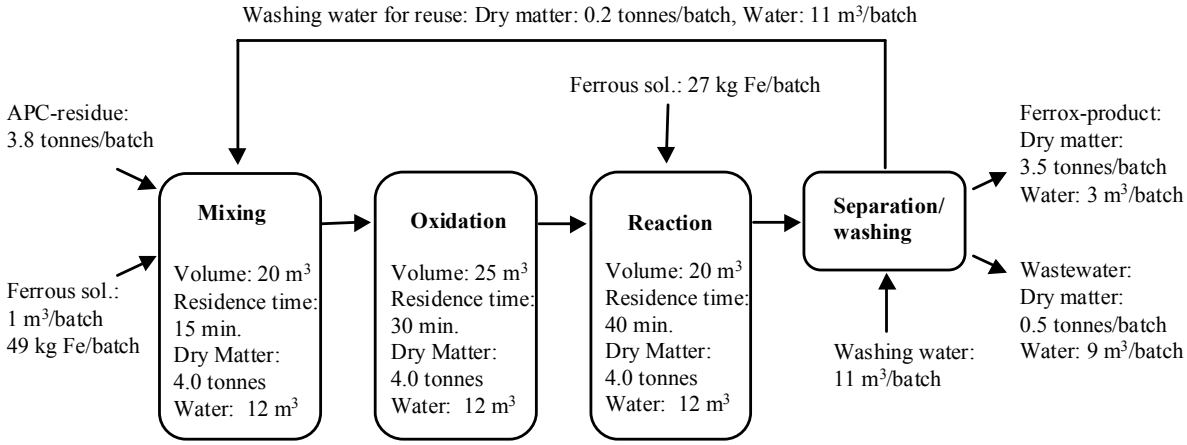

Figure 6.1. A Ferrox-treatment plant with batch-wise stabilisation of APC-residues. The figures are based on stabilisation of 10,000 tonnes fly ash per year. Each of the units mixing, oxidation, reaction and separation/washing units are separate units at the plant and the figures in each of them indicate the volume of the unit, the residence time, the content of dry matter, and water in the unit.

The resources required for a plant as shown in Figure 6.1 appear in Table 6.1. Included in table 6.1 are the resources used for treating 10,000 tonnes of semidry APC-residue and fly ash mixed with sludge at a plant that has the same configuration as shown on Figure 6.1.

Table 6.1. Resources needed for the treatment of 10,000 tonnes of residue. The need for resources is distributed on the type of residue treated. SD is a semidry APC-residue, FA is a fly ash, and FAS is a fly ash mixed with sludge. The figures are based on findings presented in [4].

	SD	FA	FAS
Water	40,000 m^3	30,000 m^3	30,000 m^3
$FeSO_4 \times 7H_2O$	2,400 tonnes	1,000 tonnes	650 tonnes
H_2SO_4	200 tonnes[1]	-	-

[1] Equal to 2 % (w/w residue).

Stabilisation of APC-residues in a batch process has been carefully examined and wastewater from a plant for batch-wise stabilisation is anticipated to be similar to the wastewater described in [4]. Thereby, the amounts of Cl and Pb leaving the plant are similar to the amounts shown in Table 6.2. From Table 6.1 and 6.2 it appears that treating semidry APC-residue requires the most resources and causes the highest emissions from the process.

Table 6.2. The amount of wastewater, Cl, and Pb removed with the wastewater produced by treating 10,000 tonnes of residue distributed on the type of residue treated. SD is a semidry APC-residue, FA is a fly ash, and FAS is a fly ash mixed with sludge.

	SD	FA	FAS
Wastewater	32,000 m^3	23,000 m^3	23,000 m^3
Cl	1700 tonnes	640 tonnes	480 tonnes
Pb	2.2 kg	0.9 kg	1.1 kg

Using a batch process has its advantages and its disadvantages. A number of these are listed below:

- The process is carefully examined and well described
- The size of the plant is larger compared to a plant for continuous operation. Hence the investment and running costs (maintenance) are larger.
- Increased risk of clogging and coating in the plant due to batch operation.
- Good control and exact residence times throughout the plant can be achieved.
- It can be operated in daytime only or on a 24-hour basis.

6.2 Continuously run Ferrox-treatment plant

The second example is a plant where the Ferrox-process runs continuously in an industrial scale. It is based on the technology described in [4] where the Ferrox-process is studied in a semi-industrial scale plant that is run batch-wise, but modified for continuous operation. The technology is shown in Figure 6.2. A continuously run plant will typically be located at the MSW incinerator. The plant is designed for continuous stabilisation of APC-residues day and night (8000 hours/year) with a capacity of 1.3 tonnes/hour. It is based on the Ferrox-process as described in [4] but modified to reflect a continuously run process. The flow is adjusted so that the average residence time in each step is the same as in the plant for a batch process. The overall design is equal to the plant for batch-wise stabilisation with the Ferrox-process previously described. Oxidation and pH-adjustment are also suggested to take place in separate units to reduce the residence time in the oxidation tank and therefore reduce size and energy consumption. Furthermore reuse of the water from the washing to be added in the mixing is included. The main difference compared to the plant for batch-wise stabilisation is the smaller volumes. The smaller volume is a result of the longer operation time per year and the higher efficiency of a continuously driven process. The volume/size of each unit is determined by the desired average residence time and the size varies due to different average residence times in the units. In the layout of the plant the volume of each unit is added 20 % for stirring (again stirring increases the volume needed because of cavitation) and an additional 20 % for unforeseen capacity

expansion. The volume of the oxidation unit is added 50 % for dispersion of air besides the 20 % for unforeseen capacity expansion.

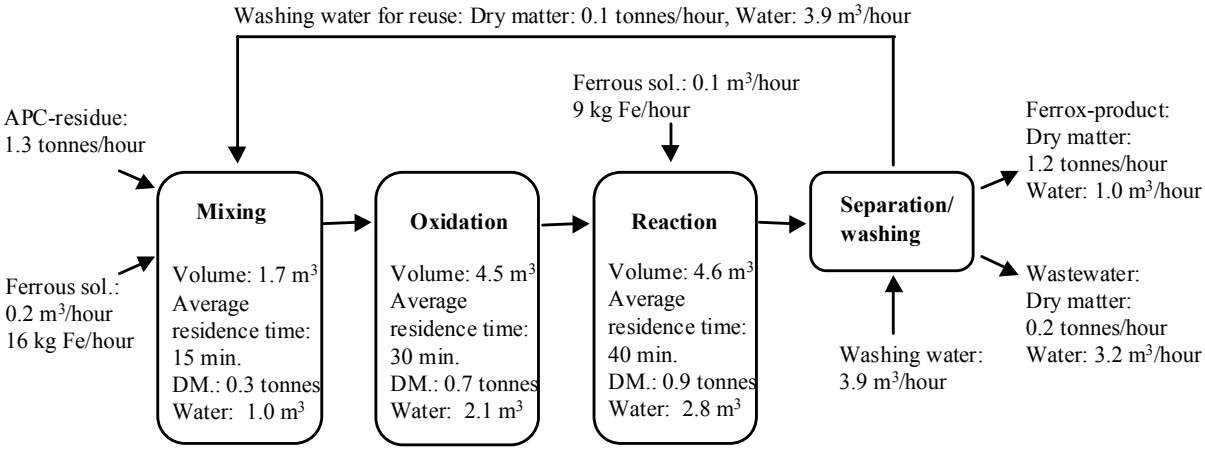

Figure 6.2. A Ferrox-treatment plant for continuous stabilisation of APC-residues. The figures are based on stabilisation of 10,000 tonnes fly ash per year. Each of the mixing, oxidation, reaction and separation/washing units are separate units at the plant and the figures in each of them indicate the volume of the unit, the average residence time, the content of dry matter (DM), and water in the unit.

A possible variation of the plant shown in Figure 6.2 is to adjust the pH in the same unit as the oxidation and carry out oxidation and pH adjustment simultaneously. Thus saving a unit at the expense of the flexibility of the plant. Simultaneous oxidation and pH adjustment have not been examined directly.

The resources (except energy) needed for a continuous process are anticipated to be the same as for a batch process. Thus, the resources shown in Table 6.1 reflect the use of chemicals and water during a continuous Ferrox-process.

The content of trace elements in the wastewater from a continuously run Ferrox-process might be influenced by the use of average residence times (based on the knowledge described in [5] and [6]) compared to the exact residence times that resulted in the wastewater described in [4]. However, based on the appearance of the curves for Pb and Cr as a function of time at steady pH (see [5], [6] and the section about pH adjustment) it can be assumed that the concentrations of Pb and Cr will not divert substantially from the results achieved in [4]. As the amount of wastewater is the same whether or not the process is being operated continuously or batchwise, it follows that the amounts of Cl and Pb released with the wastewater do not differ substantially from the amounts shown in Table 6.2.

The continuously run Ferrox-process has some obvious advantages but also some disadvantages. A number of the most essential advantages/disadvantages is listed below:

- The process is carefully examined and well described, but continuous operation has not been tried. However, there are several indications that it could be done with results that do not differ substantially from the results described so far for the batch system.
- The size of the plant is smaller compared to a batch operated plant leading to reduced investments, reduced running costs (cheaper maintenance and reduced manual work), and reduced area requirements.
- Good control during the process can be anticipated because the average residence times can easily be adjusted.
- It should be located on a site where day and night operation can be handled.

6.3 An on-site treatment and landfilling plant

The third example is based on the technology described in [3] where the Ferrox-process is studied as on-site treatment and landfilling technology using the drainage of the landfill as the separation unit. The washing step is omitted in using this technology. The plant is shown in Figure 6.3. An on-site plant operated batch-wise for stabilisation of APC-residues is thought to be located adjacent to a landfill, which is the final destination of the treated residues. At such a location it will normally only be relevant to operate the plant during the daytime.

The plant is designed for batch-wise stabilisation of APC-residues. Each batch consists of 5.7 tonnes of APC-residue. Compared to the technology described in [3], oxidation is followed by a pH-adjustment done in the same unit to keep the overall design simple (see Figure 6.1). In addition to this unit, the plant consists of a mixing tank. The separation/washing unit is omitted and the suspension is spread out directly on the surface of the landfill. The wastewater percolates through the landfilled Ferrox-products and is removed through the drainage system at the bottom of the landfill. Thereby, the Ferrox-product is left on top of the landfill and is thereby landfilled in thin layers.

The plant is designed to operate during normal working hours (1750 hours/year). The units are in use simultaneously, e.g. mixing one batch starts when another batch is still in the oxidation/reaction vessel. This is done to increase the efficiency of the plant and reduce the size of the units. The size of each unit is determined by the batch size and they are, therefore, relatively large. Again, in the layout of the plant the volume of each unit is added 20 % for stirring (Stirring increases the volume needed because of cavitation) and an additional 20 % for unforeseen capacity expansion. The volume of the oxidation unit is added 50 % for dispersion of air besides the 20 % for unforeseen capacity expansion.

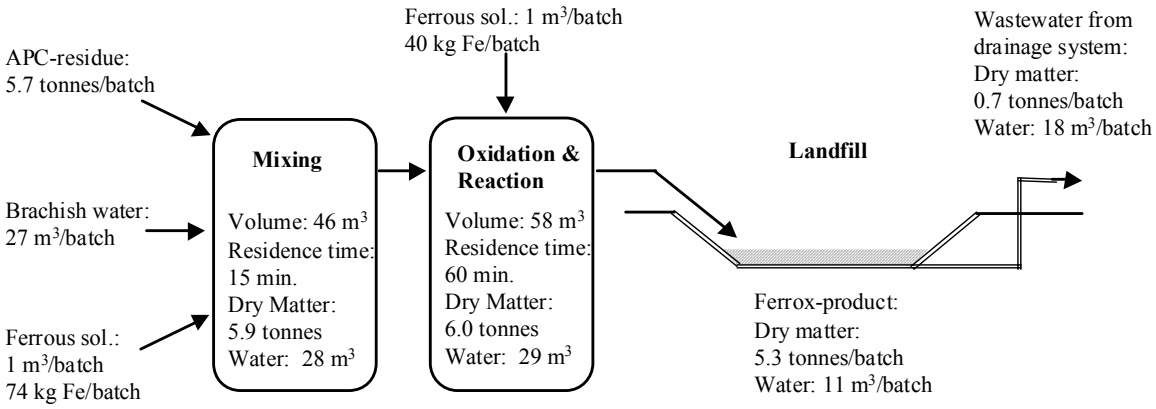

Figure 6.3. A Ferrox-treatment plant using on-site treatment and landfilling technology as described in [3] for stabilisation of APC-residues. The figures are based on stabilisation of 10,000 tonnes fly ash per year. Each of the mixing, oxidation/reaction and separation/washing units are separate units at the plant and the figures in each of them indicate the volume of the unit, the residence time, the content of dry matter, and water in the unit.

The resources needed for treating 10,000 tonnes APC-residue in a plant as shown on Figure 6.3 are similar to the resources shown in Table 6.1 with regard to chemicals. The suggested on-site treatment and landfilling use water equal to L/S 5 l/kg. Compared to the other examples outlined in this chapter the water consumption is higher (50,000 m^3) but brackish water is used as the primary water source. The use of brackish water is a modification compared to the process described in [3], which describes the on-site treatment and landfilling technology. This is done to counterbalance the higher water consumption and is an incorporation of the findings described in [2].

Stabilisation of APC-residues by on-site treatment and landfilling technology has been carefully examined in a laboratory scale and the wastewater from a plant using this technology is anticipated to be similar to the wastewater described in [3]. Thereby, the amounts of Cl and Pb leaving the plant are similar to the amounts shown in Table 6.2. As fly ash mixed with sludge is not included in the study of on-site treatment and landfilling it is not included in Table 6.3 either. From Table 6.1 and 6.3 it appears that treating semidry APC-residue requires the most resources, but releases the least Pb. In the study presented in [3], pH-adjustment during the process was not used. As a result of this, high concentrations of Cr (700-1100 µg/l) were found in the wastewater from the treatment of fly ash. The plant described is supplied with pH-adjustment (see Figure 3) but increased concentrations of Cr in the wastewater might still occur due to slow separation, during which pH cannot be controlled.

Table 6.3. The amount of wastewater, and Cl and Pb removed with the wastewater produced by treating 10,000 tonnes of residue distributed on the type of residue treated. SD is a semidry APC-residue and FA is a fly ash.

	SD	FA
Wastewater	30,000 m^3	30,000 m^3
Cl	870 tonnes	570 tonnes
Pb	1.5 kg	3.3 kg

Some of the advantages and disadvantages of the on-site treatment and landfilling are listed below. The list is not a complete list but presents the most important ones.

- The process is carefully examined and well described in a laboratory scale.
- The separation unit is replaced by the existing drainage system of the adjacent landfill.
- The sizes of the tanks are large in order to keep the plant simple and because the process is run batch-wise in the daytime only.
- Increased risk of clogging and coating in the plant due to batch operation.
- Good control and exact residence times during oxidation/reaction can be achieved.
- Problems with high concentrations of Cr in the wastewater from treatment of fly ash can arise due to the slow separation
- The physical properties of on-site treated and landfilled residues especially semidry/dry APC-residues, might be problematic, e.g. low hydraulic conductivity and low carrying capacity (see [3]).

6.4 General remark

Overall, it has been established that treating semidry APC-residue requires the most resources and causes the highest emissions during the process. Furthermore, the treatment time is longer and consequently the energy consumption and investment higher. In relation to using the Ferrox-process, it therefore seems more feasible to treat the fly ash without components from the semidry or dry acid gas cleaning system. This emphasises the need for viewing stabilisation and flue gas cleaning systems as a whole for instance by the use of green accounts.

7. RECOMMENDATIONS FOR FUTURE WORK

Based on this PhD project the following recommendations for future work can be provided.

It is concluded that the leachability of Cr is not generally improved by the Ferrox-process. As the leaching of Cr could pose a problem to the environment, means to prevent leaching of Cr have to be developed. In general, the changes in the process configuration as examined in this project did not reveal any solutions. However, the low leaching of Cr from untreated APC-residue during leaching in a column [4] could indicate a starting point for the future work on developing means to prevent leaching of Cr.

A full-scale plant for Ferrox-treatment of APC-residue could either be run batch-wise or continuously. In the chapter about full-scale perspectives, a continuously operated plant is described. However, a continuously run Ferrox-process has not been examined directly and it could, therefore, be a topic for future work. It is concluded that the leaching properties of the Ferrox-products are robust towards changes in the process configuration. Furthermore, continuously operated separation and washing units have been used successfully for APC-residues (KARA, 2001). Therefore, the main concern in relation to running the Ferrox-process continuously is the quality of the wastewater. In a continuous process the residence times for each step will only be average residence times and this could potentially affect the content of trace elements in the wastewater.

Further developments/improvements of the process could be made to reduce the running costs or investments. Oxidation and pH-adjustment could, for instance, be performed simultaneously or partially simultaneously in order to save time.

This project has not included the aspect of energy consumption of a plant applying the Ferrox-process, but such considerations are needed for estimating the operating costs. Based on the knowledge achieved in this project and experience gained from similar processes, an estimate on energy consumption can be made without any practical work. This work has partially been carried out by COWI Consulting Engineers and Planners AS, Parallelvej 2, DK-2800 Kgs. Lyngby, Denmark, but the result has not yet been published.

Given the perspective of using the Ferrox-process for stabilisation of several hundredthousand tonnes of APC-residues the long-term stability of the Ferrox-product has to be thoroughly examined. A great effort has up till now been done in this field (this PhD thesis and Sørensen, 2001). Furthermore, lysimeters have been established filled with Ferrox-product similar to those described in [4] for a further investigation of the leaching properties. However, no result from these investigations are available yet.

The lysimeters have been established by Environment & Resources DTU (former Department of Environmental Science and Engineering), Technical University of Denmark. Also, from a scientific point of view, further studies on the binding mechanisms and the factors controlling the release of the trace elements could prove interesting. A study of the stability of the iron oxides, especially with regard to the redox conditions related to a possible disposal scenario, would further document the stability of the treated residues.

Not included in the scope of this thesis, but relevant to the full-scale application of the Ferrox-process, is an identification of possible scenarios for disposal or reuse. A study of the physical properties related to the end destination/disposal scenario for the Ferrox-product is relevant. As an example, disposal on a controlled landfill is the most obvious way of handling the Ferrox-treated APC-residues on a short-term. To do so, it is necessary to examine the physical properties related to landfilling.

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VI

4. Pilot plant

This appendix is a translation of chapter 4 from Environment & Resources DTU (former Department of Environmental Science and Engineering), AV Miljø, I/S Amagerforbrænding, I/S Vestforbrænding, and Ansaldo-Vølund A/S (2001). Ferrox-projektet, Slutrapport 2. fase, January 2001. Environment & Resources DTU, Technical University of Denmark. In Danish.

The report was prepared for the funders of the Ferrox-project including the work done on the Ferrox-process in a semi-industrial scale: AV Miljø, I/S Amagerforbrænding, I/S Vestforbrænding, and Babcock & Wilcox Vølund ApS.

The actual chapter was written by Kasper Lundtorp and sums up the optimisation of the Ferrox-process in a semi-industrial scale prior to the work described in [4]. The translation is without the appendices that is a part of the original report, but which is to detailed in this context. Compared to the original version a few minor irregularities has been corrected.

This chapter describes the pilot plant and the experience gained and results achieved. Ferrox-treatments in the plant are carried out as single-batch treatments, numbered consecutively. In general, the descriptions refer to the particular trials conducted for this batch no. (e.g. B23 = Batch 23). Appendix 13 lists the measuring results of each particular batch. The appendix is composed of worksheets, but is prefaced by an outline. As appears from the number of batches, not all the results are explicitly presented in the following. There are several reasons for this:

- Initial batch for commissioning of the plant.
- Batch for the initial tests, e.g. B60, intended to demonstrate whether it was realistic to use sulphuric acid.
- Reference batch, allowing evaluation of the process en route.
- ”Training batch”, whose functions were to run in a new technique in the plant and provide training prior to documentation runs.
- Errors, of either a plant engineering or human nature.
- Batch overtaken by developments, e.g. B43.

Three different types of residues have been treated in the pilot plant:

- A semidry residue from the fabric filter at I/S Amagerforbrænding (in the following referred to as ”SD”). I/S Amagerforbrænding adds a little activated carbon during the gas cleaning besides a suspension of CaO. As a result, SD’s residue consists of fly ash, the reaction product from the semidry process, unreacted $Ca(OH)_2$ and a little activated carbon.

- Fly ash from the electrostatic precipitator at I/S Vestforbrænding (in the following referred to as ”FA”).
- Fly ash from the electrostatic precipitator at I/S Vestforbrænding mixed with sludge from the wet scrubber of the same plant, in the proportion in which they are mixed before depositing (in the following referred to as ”FAS”).

4.1 Background

Prior to the completion of the pilot-scale project, VKI (now DHI) built a pilot-scale plant for stabilisation of residues by the VKI method. To take advantage of the fact that the two stabilisation processes involve identical unit operations in major parts of the process, it was agreed that the installed plant was to be leased half the time to the Ferrox-project, which also supplied the plant with various components (e.g. a mixing tank, a ferrous tank etc.), allowing it to carry out the Ferrox-process. For the Ferrox-project, this meant that the pilot-scale plant became eight times bigger than outlined in the original project decription, but also that the plant was not planned solely with the Ferrox-process in view. From the start, the idea was for the Ferrox-process in the pilot plant to run like a batch process. In the planning phase, the aim was to make a single-batch run insofar as this was possible. This meant that a Ferrox-treatment of a batch (mixing, aeration, filtering and washing) was carried out without being split up into smaller portions during the process. In the planning phase, it became obvious that the volume of the plate-and-frame filter press was a limiting factor in the size of a batch and a governing factor in the design of other components.

4.2 Description of the plant

The plant consists of the following components:
- Receiving silo (floor 0)
- Ferrox-tank (floor 0)
- Mixing tank (floor 0)
- Process tank (floor 1)
- Filter press (floor 2)
- Spill and circulation tanks (floor 1)

The mixing tank and the Ferrox-tank, including the electric control and the data collection equipment for these, were installed in conjunction with preparation of the plant for treatment of residues by the Ferrox-method. To start with, the controlling component was the plate-and-frame filter press already installed.

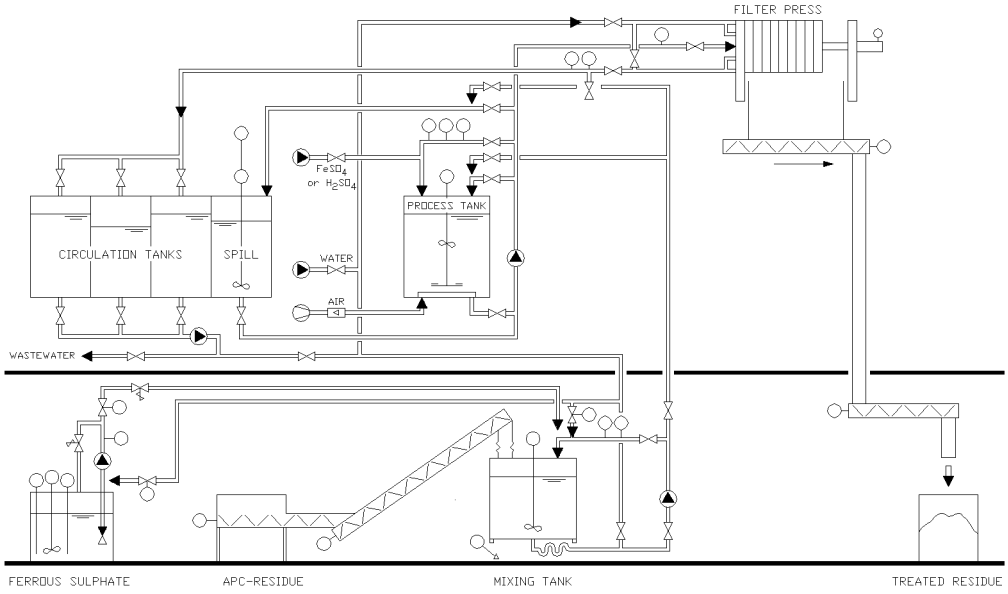

Figure 4.1. Drawing of the Ferrox-pilot plant

Figure 4.1 shows a drawing of the plant including the said units. The following describes the plant with cross-references to Figure 4.1. The description aims at giving an overview. For detailed technical descriptions, see the operational manual/documentation for the plant.

In general, all the tubes, valves and fittings are made of PVC. The pumps applied are driven by compressed air except for the metering pump of the Ferrox-tank, which is a power-operated diaphragm pump. Consequently, the compressed-air pumps do not contribute to the power consumption of the plant.

Ferrous sulphate,heptahydrate arrives on pallets carrying 40 sacks, each containing 25 kg. From there, ferrous sulphate is admixed by means of an electric tackle and a travelling grab in the Ferrox-tank. The Ferrox-tank is equipped with an agitator, a temperature sensor, a level monitor and recirculation pipes and is fitted with a dispenser pump, a densitometer and a valve positioner (engine-driven) for dispensation to the mixing tank. The Ferrox-tank has a volume of 1000 litres and is made of PE plastic. In the Ferrox-tank, ferrous sulphate,heptahydrate is mixed with water to make a strong solution of Fe^{2+}, to be dispensed to the mixing tank. The Fe^{2+} concentration is measured on-line by means of the densitometer, making use of the fact that there is an almost linear correlation between density and concentration at current concentrations,

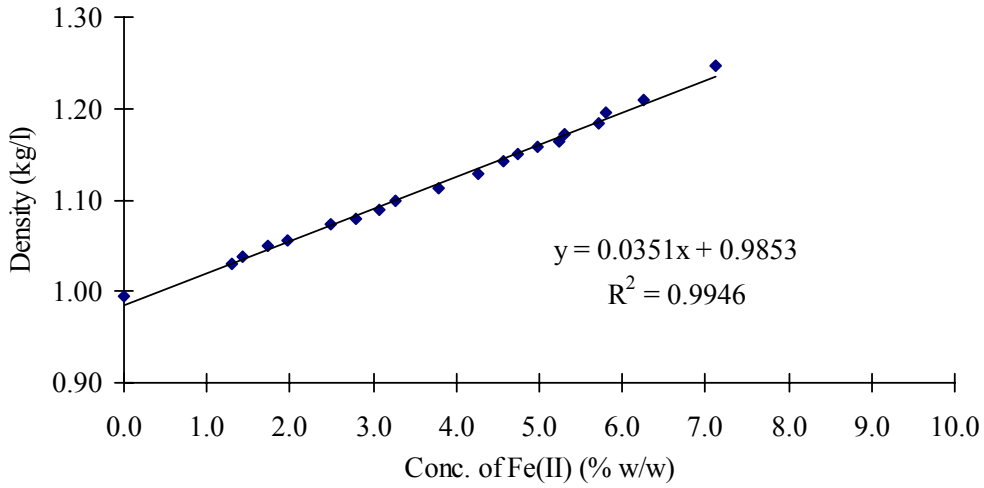

Figure 4.2. Example of a densitometer calibration curve. Density as a function of Fe(II) in samples. Please note the good regression.

which is found in various current chemical works of reference. Figure 4.2 shows an example of a densitometer calibration curve[1], depicting interconnected values of density and measured Fe concentration.

The residues arrive at the plant in mobile transport silos, each containing 2-300 kg of residue. At the bottom, the mobile transport silos have a flap, through which the residue is fed into the receiving silo. The receiving silo holds 7-800 kg maximum. The residue is dispensed via the horizontal screw conveyor M7, mounted at the bottom of the receiving silo. From M7, the residue is dispensed to a slanting screw conveyor (M8), which carries the residue up into the mixing tank. The residue is dropped through a flap supplied with an actuator, which is activated from the control panel.

In the mixing tank, the ferrous-sulphate solution is mixed with water and the residue. The tank is made of stainless steel and holds 1000 litres. The tank is equipped with an agitator, a light, a glass lid and a recirculation pipe. The recirculation pipe is fitted with a pump, pH and conductivity sensors and a valve positioner for pumping the contents to either the process tank, the filter press or the spill and circulation tanks. The tank is placed on 3 weighing cells.

The mixture of ferrous-sulphate solution, water and residue is controlled semiautomatically by a mini-PLC, the weighing cell controller and switches on a control panel installed at the mixing tank. The control panel reads out signals from the densitometer, weighing cells and pH and conductivity sensors from the recirculation pipe of the mixing tank.

[1] The densitometer has been calibrated 4 times.

The contents of the mixing tank are pumped up into the process tank (1,5 m^3), which is made of Fe with an inner coating of epoxy. In the process tank, the Fe compounds are aerated. It is also possible to inject CO_2. The tank is supplied with a dispersion aggregate (685 RPM) to ensure contact between air and liquid. The height of the tank ensures a sound dispersion, because tank height determines the contact time between air bubbles and suspension. The dispersion means that, in practice, the process tank cannot handle volumes exceeding approx. 1.1 m^3. Air and/or CO_2 are injected through an inlet at the bottom of the tank. The process tank is equipped with a recirculation pipe fitted with temperature, pH and conductivity sensors and a valve positioner for pumping the contents from the tank.

The filter press dehydrates the finished residue to a solids content of 53-59 % (w/w) [2] and washes the filter cake. The filter press is a plate-and-frame filter press, consisting of a pair of uprights (the ends), one of which feeds and draws off suspension and liquid, the other upright is movable (hydraulic). Between the pair of uprights is a set of filter frames (varying from 1 to 25, depending on the filtration volume), through which filtration is effected. The volume of filter cakes in the press when all filter frames are in use is 169 litres. At a solids content of 55% and a density of 1.5 kg/l, this equals approx. 140 kg of solids. The suspension will be pumped from the process tank into the filter press, which causes the suspension to be dehydrated on the filter cloths. The pressing is effected by pressure supplied by the pump (6-7 bars maximum). The feed pipe is fitted with a (manual) valve positioner so that water can be fed through the filter cake (the dehydrated material) and wash it. The filter press is drained manually by disassembling the frames and dumping the collected material into the casing of a horizontal screw conveyor (M2), which carries the filter cakes to a waste pipe. The waste pipe ends in a horizontal screw conveyor (M1), mounted under the ceiling of Deck 0. This screw conveyor drops the filter cakes into a container.

In the event of washwater being recirculated from the filter press, three intermediate storage tanks of 3000 litres each have been installed to catch the washwater for recirculation. There is also a tank of 3000 litres (spill tank) with two agitators (900 RPM) to catch any waste streams.

At the process tank, there is a small controlboard with a block diagram of the total process with a read-out of pH, conductivity, weight and temperature. The block diagram has on/off-switches for power to the plant and emergency stops.

All sensors except the temperature of the Ferrox-tank send their signals to a PC, which collects data. This means that the following is logged:

- Conductivity in the mixing tank

[2] Herein, solids mean the weight of solids in proportion to the weight of solids + liquid.

- pH in the mixing tank
- Weight of the mixing tank
- Density of the Fe solution
- Conductivity in the process tank
- pH in the process tank
- Temperature in the process tank
- Conductivity of filtrate from the filter press
- pH of filtrate from the filter press

4.3 Experience gained

The plant has been in commission for a year. During that time, much experience has been gained and the most valuable will be described in this paragraph. In general, the functionality of the mixing tank and the Ferrox-tank came up to expectations, based on the purchase specifications. The dimensions of the installed mixing tank and Ferrox-tank fit (as expected) the maximum volume of the plate-and-frame filter press. Fitting in the new components and readjusting the plant from one treatment option to another have not posed any problems. The selected materials seem to be of high quality, and no corrosion or the like has been found. The data collection is comprehensive and aptly reflects the process. Appendix 14 describes a Ferrox-treatment of a residue in the pilot plant, based on a printout of the data collection and observations made en route. The description in Appendix 14 also includes the experience gained about various process parameters. Beyond the general positive picture, there have been both positive and negative lessons to be learned from the plant as a whole. The most important are listed below:

- Treatment of 170 kg of the SD residue or 180 kg of the FA residue is the maximum batch size that the filter press can manage at a time.
- It has proved difficult to transfer the residue from the transport silo to the receiving silo solely by gravitational pull. Mounting a vibrator in the plant has solved the problem.
- The slanting screw conveyor (M8) can transport semidry residues and dry fly ash, but blocks up when having to transport wet residues. It should be noted that the slant of the screw conveyor is more oblique than normally recommended.
- After calibration and commissioning, the dispensing system, which is based on weighing cells, has proved very precise (uncertainty: < 1 kg).
- It requires intensive agitation to keep the residue in the mixing tank in suspension.
- The ball plug valves tended to get stuck towards the end of the project period.
- On-line metering of the Fe concentration is feasible, with an uncertainty < 1%.
- Filtering/pressing takes 5-10 min. The solids content obtained is 53-60%.
- The design of the air inlet of the process tank may pose problems in the form of blocking if no allowance is made for this in the design. However, dispersion seems

to be independent of the air inlet design so long as it is positioned directly below the dispersion aggregate.

- Washing the Ferrox-product causes considerable leakage from the filter press (up to 25% of the total washwater consumption). The leakage is caused by water being forced out between the filter frames. This means that the leakage water does not pass through the Ferrox-product to wash it. The problem is solved by metering the leakage flow and deducting the result from the total washwater consumption.
- On-line conductivity metering in a residual-product suspension is not unproblematic because current conductivity sensors block up. The problem is solved by means of an ”open” type with graphite electrodes.

4.4 Resource considerations

The Ferrox-treatment consists of mixing a residue with a ferrous-sulphate solution, followed by aeration of the suspension. Lastly, the Ferrox-product is separated from the water.

During the Ferrox-process, the following resources are consumed:

- Water
- Ferrous sulphate,heptahydrate
- Energy
- Time
- In addition, sulphuric acid in the treatment of SD, which is disregarded in the following paragraphs.

The following presents a rough estimate of the various resources consumed and the materiality of the said consumption in proportion to the total economy of the process.

Water costs DKK 16.38 per m^3 [3] and, with the water consumption equalling L/S 3 l/kg, the cost is DKK 50 per ton. If a refund of the water tax is obtained, the cost of pure water is DKK 30 per ton. In addition to the direct cost, water consumption has a negative effect on the green accounts. At Vestforbrænding, it is possible to use second-rate water instead, at a price of DKK 0.60 per m^3 [4], which amounts to DKK 2 per ton. To this is added an effluent charge of DKK 12.75 per m^3 [5]. Including effluent charges, the cost of water comes to DKK 40 per ton. Effluent charges depend on whether a plant

[3] The price paid by Vestforbrænding for pure water including VAT and tax (DKK 6.25/m^3). Stated by Vestforbrænding on 29 July 1999.

[4] The price paid by Vestforbrænding for second-rate water. Stated by Vestforbrænding on 29 July 1999.

[5] The price paid by Vestforbrænding for effluents discharged to the sewer. Stated by Vestforbrænding on 29 July 1999.

is situated so that its effluents can be discharged directly into a marine recipient. The total cost of water is very dependent on local conditions, but is estimated to be between DKK 40 per ton (as is the case of Vestforbrænding) and DKK 70 per ton (if the full price is paid for both water and effluent, but including a refund of the water tax).

Ferrous sulphate,heptahydrate is a by-product of titanium extraction, and the least expensive quality costs DKK 400 per ton EXW [6]. To this is added freight (lorry) at DKK 200 per ton [6]. In total, DKK 600 per ton. For each ton of residue, 13-49 kg Fe, equalling 65-245 kg of Fe compound for each ton of residue. The cost of the Fe compound will thus be DKK 45-180 for each ton of residue, depending on the residue treated.

Energy is consumed by screw conveyance of residues, by the pumps, dispersion/aeration, the filter press and various types of monitoring. At an estimate, dispersion/aeration consumes the largest amount of energy, followed by the energy consumed by the pumps. Dispersion/aeration consumes approx. 30 kWh/ton, assuming that dispersion takes 30 minutes. The price of one kWh is DKK 0.709 [7], resulting in an electricity cost of DKK 21 for dispersion. The total cost of energy is estimated at less than DKK 40 per ton.

The time consumed on processing is an important factor in the capacity of a plant and also in the requisite size of a plant. Time also affects the cost of manning a plant. The estimated processing time for fly ash is as follows:

- 30 min. Mixing Fe(II) with a residue, and precipitation time until pH > 10.
- 20 min. Dispersion/aeration of a suspension.
- 40 min. pH adjustment and reaction time
- 10 min. Filtration
- 20 min. Washing of the Ferrox-product

In addition, time is consumed on pumping.

The above paragraph and Figure 4.3 illustrate the most time-consuming sub-processes. Based on these diagrams, the focus should be on the mixing cycle, the dispersion time and the reaction time. But, in terms of time consumption, it does not pay to optimise the filtration. For the SD residue, the total time will be one hour longer.

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[6] Stated by Dankalk A/S on 28 July 1999.

[7] The price paid by Vestforbrænding in the daytime, including a sulphur charge and the portion of the CO_2 charge paid by Vestforbrænding. No electricity charge is included because it is deductable for Vestforbrænding. Stated by Vestforbrænding on 29 July 1999.

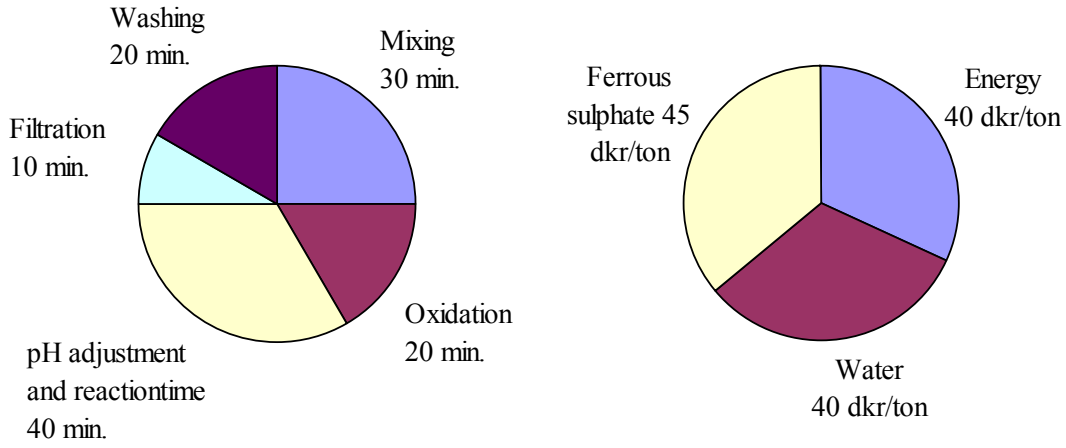

Figure 4.3. A breakdown into minutes and DKK/ton of the time and cost incurred in a Ferrox-treatment of the FA residue. A full circle represents 2 hours or DKK 125/ton.

Figure 4.3 illustrates a breakdown of the costs incurred in treating the FA residue. As regards treatment of the SD residue, the total cost will be approx. DKK 340 per ton, because the consumption of water (DKK 30 per m^3), chemicals and energy is higher. The cost of ferrous sulphate will dominate by DKK 180 per ton. The total cost of Fe compound and water is the most important factor in the treatment of 1 ton of APC-residue. It is therefore important that the Fe dosage is correct in relation to stabilisation as well as resource consumption. The Fe dosage has been thoroughly researched in the laboratory. The possibilities of recirculating water in the pilot plant have been examined. In addition, the time consumption is an important parameter. However, a reduction in energy consumption does not seem feasible, which greatly affects the price of treating 1 ton residue and is therefore given priority after an optimisation of the chemicals, water and time consumed by operating the pilot plant.

4.5 Analysis of Ferrox-product sampling

The Ferrox-treatment is carried out in batches of 170-190 kg each. Since only up to 100 g of the finished Ferrox-product is leaching tested, a sampling covers less than 0.1 % of the treated material. Sampling is consequently an important parameter in the evaluation of results. The following describes a test of the sampling to find the most efficient procedure.

In filtration, the suspension is fed into the vertical filter frames (numbered 2-26) of the plate-and-frame filter press. The product on the filter is subsequently washed by water fed through the frames. This procedure may result in inhomogeneous filter cakes, making it imperative to know where in the plate-and-frame filter press a sample is taken, both in terms of the frame from which the sample is taken and in terms of the

spot on the filter frame from which the sample is taken (each filter frame measures 63x63 cm). To analyse this, samples of the Ferrox-product have been taken from different frames in the filter press and from different spots on the same frame. The results are used to determine a reasonable sampling procedure. The test was conducted on Batch 6, where samples were taken from filter frames 2, 5, 11, 14 (top of the frame), 14 (mid-frame), 14 (bottom of the frame), 17, 23 and 26. All the samples were taken from the middle of the filter frame unless otherwise stipulated. The samples have been measured for dry matter content and density. In addition, the samples from frames 2, 14 and 26 have been tested for leaching by means of a pH-static test (pH 9, L/S 10 l/kg, 24 hours), and the samples have been analysed for Cl, K, Pb, Cd and Cr.

Apparently, there are minor variations in both solids and density between the various frames and depending on the spot from which a sample is taken (cf. Table 4.1). Apparently, there is no correlation between the frame in the plate-and-frame filter press (the number of the frame) and the variations observed. The difference between the solids content at top and bottom of a frame seems reasonably constant. Not surprisingly, there is a distinct correlation between density and dry matter content (high dry matter content = high density).

As appears from Table 4.2, there are minor variations in the levels of easily leachable components, such as Cl^- and K, in samples taken from different frames. This indicates either that there are minor variations in the Ferrox-product pumped into the frames or that washing is not completely homogeneous. The latter is probably the deciding factor, considering the relatively homogeneous heavy-metal concentrations.

Table 4.1. Solids percentage and density of filter cake samples taken from different spots in the filter press.

Sample	Solids %	Density g/ml
Frame 26, middle	52	1.46
Frame 23, middle	49	1.45
Frame 17, middle	48	1.40
Frame 14, top	50	
Frame 14, middle	54	1.52
Frame 14, bottom	52	
Frame 10, middle	51	1.47
Frame 5, middle	50	1.43
Frame 2, middle	51	1.48

Table 4.2. Result of pH-static leaching (pH 9 test) of samples taken from different frames in the filter press from Batch 6.

Sample	Cl^-	K	Pb	Cd	Cr
	mg/l	mg/l	µg/l	µg/l	µg/l
Frame 2, middle	650	82	< 5	6.6	540
Frame 14, middle	1600	200	< 5	10	520
Frame 26, middle	300	36	< 5	7.4	830

Based on the results shown, sampling drawing on a single frame should be considered a random sample. This form of sampling has been chosen over a composite sample taken from several frames, for practical reasons and because variations are primarily caused by inhomogeneous washing. In addition, variations are to be expected because of variations in the residues treated. Sampling of the definitively optimised product from the pilot plan should draw on several different batches.

4.6 Washwater flow

The Ferrox-product is washed in the filter press immediately after filtration. The purpose is to extract easily leachable salts from the Ferrox-product. Water fed through the filter press to wash the Ferrox-product is called washwater.

Assumably the salinity of the washwater was initially determined by the solubility of easily soluble compounds, such as chloride salts. After leaching the chloride salts, the conductivity is controlled by salts with a lower solubility, such as gypsum and carbonates, and by diffusion-controlled leaching of e.g. chloride salts. The conductivity of the first washwater is consequently expected to fall rapidly, to level off at an increasing L/S ratio.

Washing of the Ferrox-product affects the leaching of salts, such as Cl, Na, K from the finished Ferrox-product. Moreover, the lower concentration of complexing agents (e.g. Cl^-) in the percolate could also reduce the leaching of trace metals. Washing requires water, energy and time, and the consumption of these resources should be balanced against the amount of salts removed. In the plant, it is possible to vary the volume and flow of washwater. To optimise the washing process, it is analysed, as an effect of the flow. The method used in the analysis is to vary the wash flow during a number of Ferrox-treatments. During washing, samples of the washwater are taken at intervals. This method has been used on both the SD residue (Batches 14, 15 and 17) and on fly ash (FA) (Batches 21, 22 and 24). Figure 4.4 shows the conductivity as a function of the consumption of washwater, expressed by the L/S ratio. The conductivity is seen to fall rapidly to an L/S ratio of approx. 3-4 l/kg. Figure 4.4 also shows that different

washwater flows produce almost identical curves. This means that the fall in conductivity does not depend on the washwater flow.

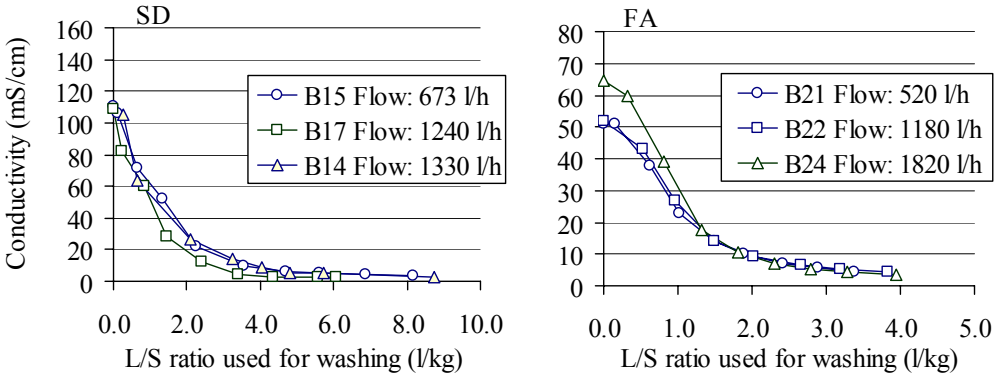

Figure 4.4. Conductivity of the washwater during washing of Ferrox-products in the filter press as a function of washwater consumption, expressed as the L/S ratio at different washwater flows. SD is the semidry residue from Amagerforbrænding, and FA is fly ash from Vestforbrænding.

Figure 4.5 shows the amount of removed chloride as a function of the washwater consumption, expressed by the L/S ratio. The figure also shows the various phases of chloride leaching. Appendix 15 shows the corresponding figures for Na and K. Irrespective of the washwater flow, washing a FA-based Ferrox-product by means of washwater corresponding to an L/S ratio of 2 l/kg can be seen to remove the majority of chloride salts. Further washing will only remove marginally more chloride, but according to Figure 4.4 other salts are removed, since washing until L/S 3 l/kg produces a fall in conductivity. Likewise, washing of an SD-based Ferrox-product by means of washwater equalling an L/S ratio of 4 l/kg will remove the majority of chloride salts. Further washing has only a marginal effect on both conductivity and chloride removal. The leaching of Na and K shown in Appendix 15, has behaviour similar to that of chloride. There are, however, considerable variations in the amounts leached from the various Ferrox-products.

The figures show that the flow is not essential to the removal of chloride. This can be seen from the fact that the paths of the curves are identical and level out at approximately the same L/S value. It should be noted that the level-out levels may vary owing to variations in the residues used for the various batches. This is, for instance, the case in Batch 17 compared to Batch 14 and 15.

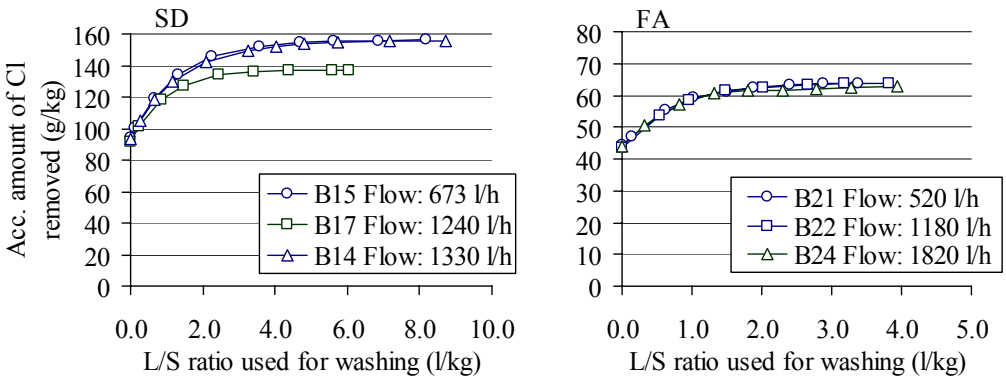

Figure 4.5. Chloride removal during washing of Ferrox-products in the filter press as a function of wastewater consumption, expressed as the L/S ratio at different wastewater flows. SD is the semidry residue from Amagerforbrænding and FA is fly ash from Vestforbrænding.

Table 4.3 illustrates the concentration in the washwater discharged from the filter press after washing until L/S 3 l/kg at different washwater flows. From this it can be seen that generally there is a higher level of chloride in washwater from the SD residue and that the concentration levels are identical for each residue. The same applies to the relative concentration (relative to the concentration at L/S 0 l/kg corresponding to the wastewater), especially for washing of fly ash from FA. So there is no clear correlation between the washwater flow and the relative removal of chloride.

Table 4.3. Concentration of chloride in washwater after washing until L/S 3 l/kg of Ferrox-products washed at different washwater flows, and the relative concentration in relation to the wastewater concentration. SD is the semidry residue from Amagerforbrænding and FA is fly ash from Vestforbrænding.

	SD			FA		
	670 l/h	1240 l/h	1330 l/h	520 l/h	1180 l/h	1820 l/h
Cl^- (mg/l)[1)]	4400	2000	5400	663	665	580
Relative conc. Cl^- (%)	9.4	4.2	11.5	3.0	3.0	2.6

[1)] The concentrations are found by linear regression between the individual measuring points.

Since the washwater flow appears to have no significant effect on the salt removal, there is a free choice of washwater, taking into consideration other factors, such as time consumption.

4.7 Oxidation time

An important step in the Ferrox-process is the aeration, during which some of the Fe(II) hydroxides are reacted into Fe(III) oxides. To examine the aeration process and determine the optimum oxidation time, the Fe(II) concentration is monitored in the suspension during the process in the pilot plant. Some of the Fe(II) is expected to react already in the mixing tank, but most of the oxidation takes place in the process tank, into which air is injected.

The test is conducted as three Ferrox-treatments (two on SD, B12 and B16, and one on FA, B33). During oxidation, samples are taken at various intervals from the suspension in the process tank. The samples are taken so headspace is avoided and sealed immediately after sampling and placed on ice. The samples are extracted by means of perchloric acid the same day and analysed for Fe^{2+} and Fe-total.

In Figure 4.6, the oxidised portion of the originally added Fe(II) quantity is shown as a function of the oxidation time for Ferrox-products based on SD and FA.

The results show that the process is almost identical from one time to another. On Figure 4.6, the process is only shown until three hours after the start of aeration. The process is tested until 24 hours after start of the aeration. The result of this show that the oxidation almost stops within the first couple of hours.

Figure 4.6 shows that the optimum aeration time for an SD-based Ferrox-product is approx. 50 minutes and, for a FA-based residue, it is approx. 15 minutes. In both cases, the result is oxidation of approx. 70 % of the Fe quantity originally added.

Figure 4.7 shows the dispersion efficiency, i.e. the oxygen uptake efficiency, which is seen to be at its maximum after 10 minutes for Ferrox-treatment of FA and 35-51 minutes for SD. The dispersion efficiency, as expressed herein, is a measurement of the oxidation achieved by the energy consumed by the injection of air. If the choice of optimum aeration times is compared with the times of maximum dispersion efficiency, we see that there is a sound correlation between the various optima. This means that, if aeration times of 50 and 15 minutes for SD and FA, respectively, are chosen, there is a sound utilisation of the injected air and the energy consumed by aeration. However, this applies to the installed plant only if dispersion is set at approx. 675 RPM and injection at approx. 65 m^3 air/time.

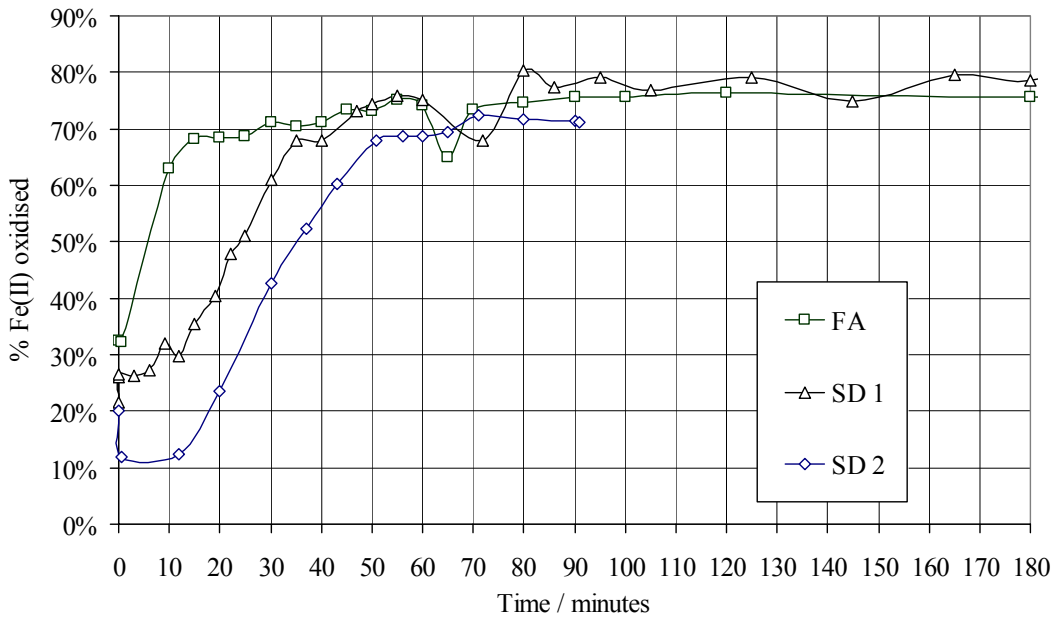

Figure 4.6. Ferrox-treatment of a semidry residue (SD) and fly ash (FA). % Fe(II) oxidised in proportion to Fe(II) added with the ferrous sulphate as a function of time. Zero minutes equal the point in time when the suspension is pumped up into the process tank and the aeration starts.

In connection with the test made of the oxidation time, it was necessary to establish a method for extraction of Fe(II) from the Ferrox-suspension. After many investigations, the result was that an extraction by means of 1 M perchloric acid does not affect the Fe(II)/Fe(III) balance. Appendix 16 shows the measuring results of selected samplings for Fe(II) and Fe-total extracted by means of 1 M perchloric acid, and Fe-total extracted by means of 7 M HNO_3. The conclusion drawn from the measurements in Appendix 16 suggests that 1 M perchloric acid extracts only Fe(II) in the Ferrox-suspension. Based on this test, it is not possible to determine whether all the Fe(II) is extracted, but there is every likelihood of this, considering the consistent results of the aeration test. In addition, the Fe(II) in the suspension is bound in various amorphous compounds that are less resistant to acid than the more crystalline Fe(III) minerals, and these amorphous compounds are likely to dissolve in perchloric acid.

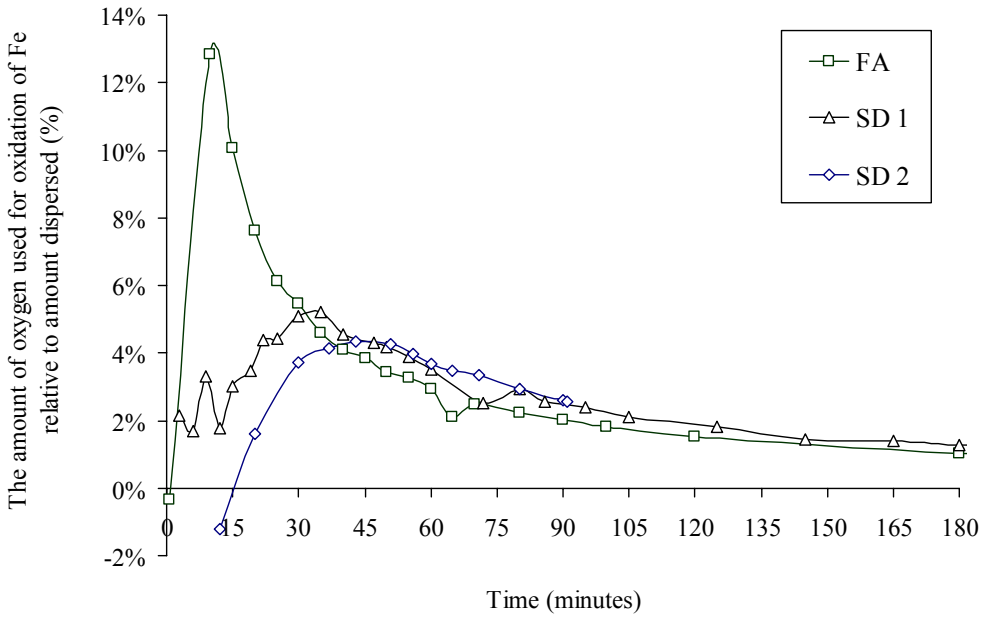

Figure 4.7. Ferrox-treatment of a semidry residue (SD) and fly ash (FA). Dispersion efficiency expressed as the percentage of O_2 consumed in proportion to the total amount of O_2 injected during aeration as a function of time.

4.8 pH control

During the first months of running the pilot plant, the concentrations of Pb found in the wastewater, the washwater and, to some extent, in a pH static leaching test of the stabilised material, have been very inconsistent and often high, compared to laboratory tests. One explanation of this could be that, during aeration and the subsequent filtration and washing, the pH level is high (for SD 11.7-12.2 and for FA 12.2-12.8). Three different methods of reducing the pH have been investigated:

- Aeration of the suspension by means of CO_2.
- Addition of $FeSO_4$ during dispersion.
- Addition of H_2SO_4 during dispersion.

The purpose of reducing the pH is to reduce the Pb content of the wastewater, i.e. the water filtered off and discharged, without causing an uncontrollable increase in the concentration of other trace metal. This means that the pH level must be controlled during filtration, which takes approx. three minutes immediately after aeration. However, the pH found in the washwater from the subsequent washing is less important, since this water tends to be recirculated during the process. Any trace metal will then be part of the subsequent Ferrox-treatment.

4.8.1 CO_2

Based on the above, a test was made to determine which pH level produces the lowest trace metal content in the wastewater, when dispersed by means of CO_2-enriched air after ordinary aeration. The test is conducted by Ferrox-treating five residues (two from Amagerforbrænding – Batches 25 and 26, two from Vestforbrænding – Batches 23 and 38, and one mixed with sludge from Vestforbrænding – Batch 41). After aeration by means of atmospheric air, the dispersion continues with air enriched with CO_2 (5 %). This causes a decrease in the pH of the aerated suspension. From the suspension, samples have been taken at different pH values after the relevant pH value has been maintained for approx. 10 minutes. The samples are filtrated immediately after sampling so that a sample reflects the wastewater at the given pH. The samples are analysed for Pb, Cd and Cr. Below is shown the content of Pb, Cd and Cr in the wastewater, shown as a function of the pH during treatment of residues from Amagerforbrænding and Vestforbrænding.

Figure 4.8 shows the concentrations of Pb, Cd and Cr at different pH values in the suspension. It will be seen that the concentration of dissolved matter for all three elements is obviously dependent on the pH level. The concentration of Pb falls at a falling pH. This means that the concentration in the wastewater is high before aeration with CO_2, but falls to below 100 µg/l at approx. pH 10.5. For FAS, however, the Pb concentration falls to < 100 µg/l at pH 11.2. Cd increases at a falling pH. The Cd concentration is below 10 µg/l for a pH > 10.25 during treatment of the SD residue and the FAS residue and for a pH > approx. 11 during treatment of the FA residue. The concentration of Cr increases at a falling pH. The concentration level during treatment of SD is very low (below 100 µg/l) for a pH > 9, while the Cr concentration in the wastewater during treatment of the FA residue increases to over 100 µg/l at pH 10-11.5. The concentration level of Cr varies considerably in the two tests of the FA residue (Batch 23 and 38). The deciding factor could be variations in the residues applied. For FAS, the Cr concentration increases to over 100 µg/l at pH 9.8.

Based on Figure 4.9, it is possible to determine the optimum pH value of the wastewater during filtration. Determination of this pH value will be a balance of the acceptable amounts of the various trace metals in the wastewater. For treatment of the SD residue, the optimum pH value will be approx. 10.3, while Pb is below 100 µg/l, Cr is below 50 µg/l and Cd is approx. 5 µg/l. For treatment of fly ash from FA, the corresponding optimum pH value will be approx. 10.7, while Pb is approx. 40-170 µg/l, Cr is 40-400 µg/l and Cd is approx. 10 µg/l. The Cd concentrations obtained are slightly higher (approx. twice higher) than those obtained in the laboratory. Likewise, the Pb concentrations are slightly higher (approx. 2-6 times) during treatment of the FA residue than those obtained in the laboratory. On the other hand, Cr is 5-50 times lower than the result of laboratory tests of the FA-based Ferrox-product. For fly ash mixed with sludge,

the optimum pH level at pH control/adjustment by means of CO_2 is approx. 11.0, while the Pb concentration is below 100 µg/l and the Cd concentration is low (3 µg/l). The Cr concentration is below 100 µg/l up to pH < 10 and fall at an increasing pH level.

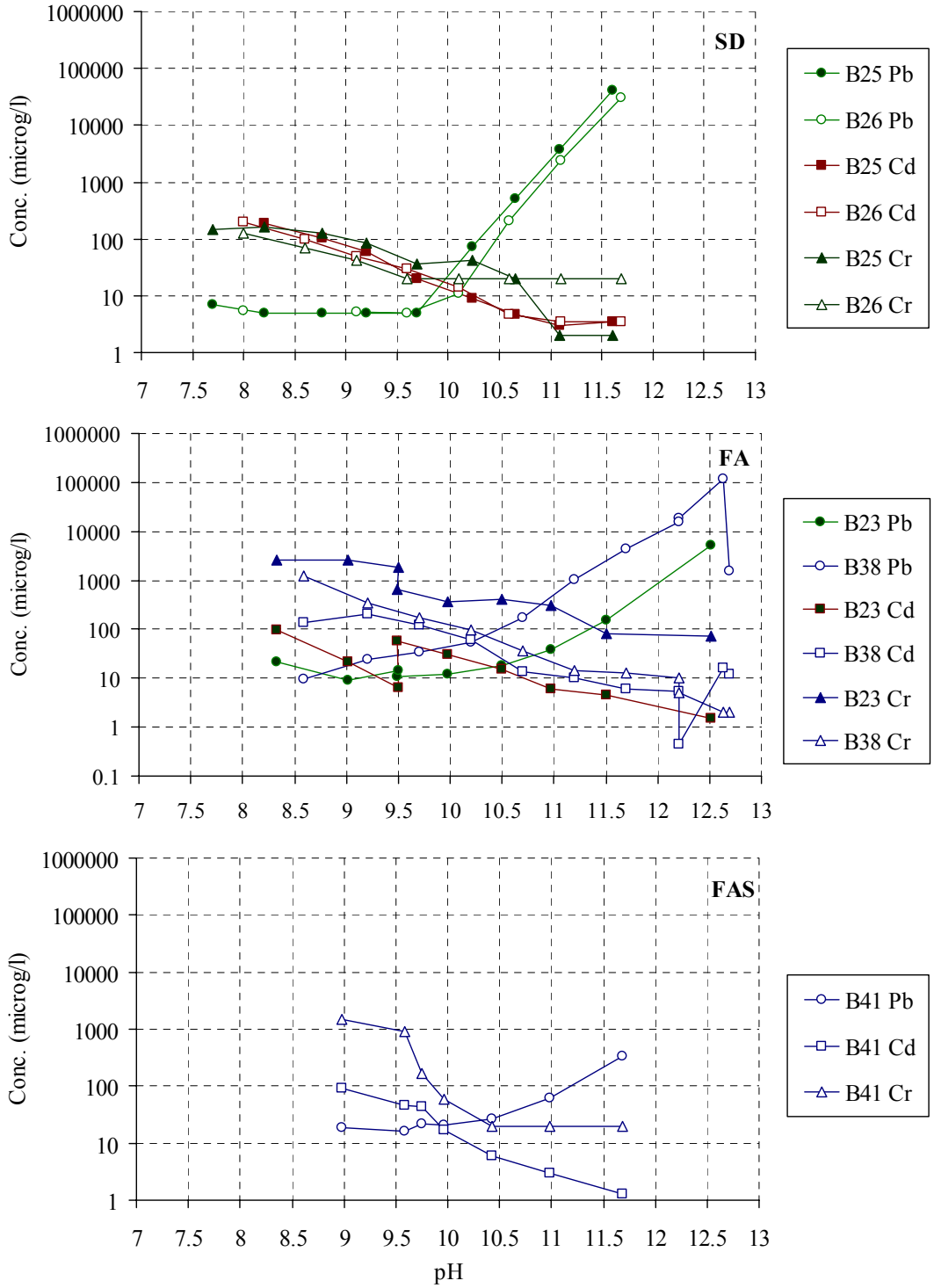

Figure 4.8. The concentrations of Pb, Cd and Cr in the wastewater as a function of pH in the suspension during stepwise addition of CO_2. SD is the semidry residue from Amagerforbrænding, FA is fly ash from Vestforbrænding and FAS is fly ash from Vestforbrænding mixed with sludge.

These results have been found by batch testing. If variations in the residues shift the concentration curves in Figure 4.8, this could change the resultant concentrations, owing to the relatively narrow interval in which the concentrations of Pb, Cd and Cr are moderate.

The effect on the leaching properties of the stabilised material is seen in Table 4.4, from which it appears that a reduction in the wastewater pH may reduce the leaching of Cd. However, the variations are no bigger than could be explained as the variations between two different Ferrox-treatments, and the result is therefore only an indication. There has been no Ferrox-treatment of FAS without a pH adjustment.

Table 4.4. Results of a pH 9 test (pH-static at pH 9, L/S 10 l/kg, 24 hours) of various Ferrox-products from the pilot plant with and without CO_2 aeration.

Basis	SD		FA	
Batch	B25 + CO_2	B18 - CO_2	B38 + CO_2	B21 - CO_2
pH at filtration	9.0	12.1	9.9	12.7
Pb (µg/l)	< 5	< 5	< 5	11
Cd (µg/l)	0.9	10	5	13
Cr (µg/l)	360	160	370	1500

4.8.2 $FeSO_4$

As an alternative to using CO_2 to reduce/control the pH level, tests have been made to add $FeSO_4$ to the process tank after aeration. The process configuration has not been changed, which means that the $FeSO_4$ added to the process tank for pH adjustment is surplus to the amount mixed with the residue in the mixing tank. The test was carried out by Ferrox-treating four residues (two on SD residues – Batches 48 and 49, and two on FA – Batches 50 and 51). After aeration with atmospheric air, the dispersion of air continued with stepwise addition of small amounts of an $FeSO_4$ solution. This caused a fall in the suspension pH owing to the reaction between Fe^{2+} and OH^-. Samples were taken from the suspension at different pH values, after the relevant pH value had been maintained for approx. 10 minutes. The samples were filtrated immediately after sampling so that the test reflected the wastewater at the given pH. The samples were analysed for Pb, Cd and Cr. A similar test has been made with fly ash mixed with sludge (FAS), but in that case four separate Ferrox-treatments were made, in which the pH was adjusted by adding $FeSO_4$ at different pH values for each treatment. In this way, only one sample was obtained from each treatment. Below is shown the content of Pb, Cd and Cr in the wastewater as a function of the pH during treatment of residues from Amagerforbrænding and Vestforbrænding (both pure fly ash and fly ash/sludge).

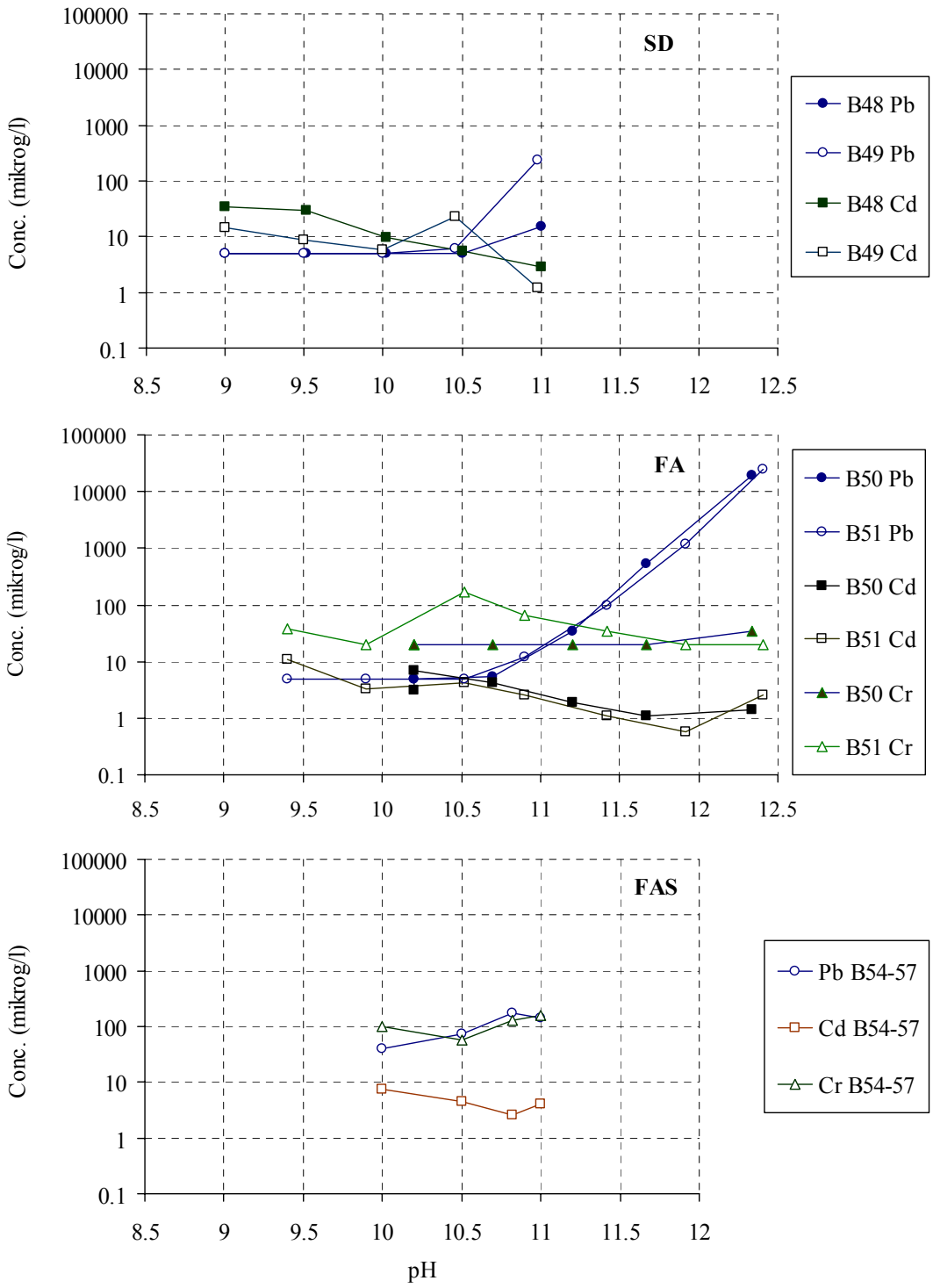

Figure 4.9 The concentrations of Pb, Cd and Cr in the wastewater as a function of the pH in the suspension during stepwise addition of $FeSO_4$. SD is the semidry residue from Amagerforbrænding, FA is fly ash from Vestforbrænding and FAS is fly ash mixed with sludge from wet scrubbing at Vestforbrænding. Cr is not included in the figure illustrating the semidry residue owing to the low chrome content of the wastewater during treatment of the semidry residue.

Figure 4.9 shows the concentrations of Pb, Cd and Cr at different pH values in the suspension. For all three elements, the concentration of dissolved metal is seen to be clearly dependent on the pH level, in the same manner as in pH control by means of CO_2. Based on Figure 4.9, the optimum pH values for the wastewater could be 10.4 for SD, 11.0 for FA and 10.5 for FAS. These values are chosen to ensure that Pb is below 100 µg/l (the Pb curve steeples around 100 µg/l) and that Cd is below 10 µg/l, preferably lower.

Compared to the test of pH control by means of CO_2, there is no significant shift in the paths of the curves for SD. For FA, a larger "pH window" has been obtained, in which the concentrations of Pb, Cd and Cr are low. This means that, compared to CO_2, $FeSO_4$ produces better results in terms of wastewater quality during treatment of FA. For FAS, the optimum pH has shifted from 11.0 to 10.5.

The effect on the leaching properties of the stabilised FA is seen from Table 4.5, from which it appears that a reduction in wastewater pH may reduce leaching of Cd, but increase leaching of Cr. The disparities are, however, no bigger than could be expected between two different Ferrox-treatments, and the result is consequently only an indication.

Table 4.5. The results of a pH 9 test (pH-static at pH 9, L/S 10 l/kg, 24 hours) of FA Ferrox-products from the pilot plant with and without $FeSO_4$ aeration.

Basis	FA	
Batch	B45 + $FeSO_4$	B21 - $FeSO_4$
pH at filtration	10.8	12.7
Pb (µg/l)	< 5	11
Cd (µg/l)	7.5	13
Cr (µg/l)	930	1500

Table 4.5 shows that leaching of Pb from the Ferrox-product is insignificant. Leaching of Cr is on a par with previous results obtained in the laboratory. However, leaching of Cd is slightly higher (approx. twice) than the result obtained in the laboratory.

4.8.3 H_2SO_4

Using $FeSO_4$ for pH control means a consumption of $FeSO_4$ in addition to the amount added in the mixing tank. In the tests of the reaction time (described later), it became clear that in some cases, during pH control of the semidry residue, close to 5% (w/w) Fe is used in addition to the 5% (w/w) added at the start of the process. The additional consumption by treatment of fly ash and fly ash mixed with sludge was much smaller

(between 0.03–0.7 % (w/w) Fe). Since $FeSO_4$ is one of the principal costs incurred by the Ferrox-process, H_2SO_4 has been tested as a substitute. H_2SO_4 neutralises the alkalinity (contrary to $FeSO_4$ and CO_2), which – other things being equal - should be maintained, because the alkalinity has a positive effect on leaching in the long term. Semidry residues have, however, such a neutralising capacity that an alkalinity equalling approx. 5% Fe is bound by the initial addition of Fe. Moreover, part of the alkalinity is carbonated and bound during aeration. So only any excess alkalinity will be neutralised, which is considered justifiable, also with respect to the long term properties.

The test is carried out in the same manner as was the test of $FeSO_4$ as a pH-controlling additive, but with the addition of concentrated sulphuric acid of a technical quality. Only in connection with SD has sulphuric acid been tested. The result is shown in Figure 4.10, in which the heavy-metal concentrations are depicted as a function of pH. As will appear, the optimum pH level is between 10 and 10.5. Between these levels, the Pb concentration falls to below 100 and the Cd concentration does not exceed 10 µg/l. Subsequent tests will have to give more precise indications of the pH at which the Pb concentration falls to below 100 µg/l, since a linear process cannot be expected. Compared with the tests of CO_2 and $FeSO_4$, the additive used to regulate the pH level is seen to be of no great consequence to the behaviour of the heavy metals. For all three additives, the optimum pH level for the SD residue is between 10 and 10.5.

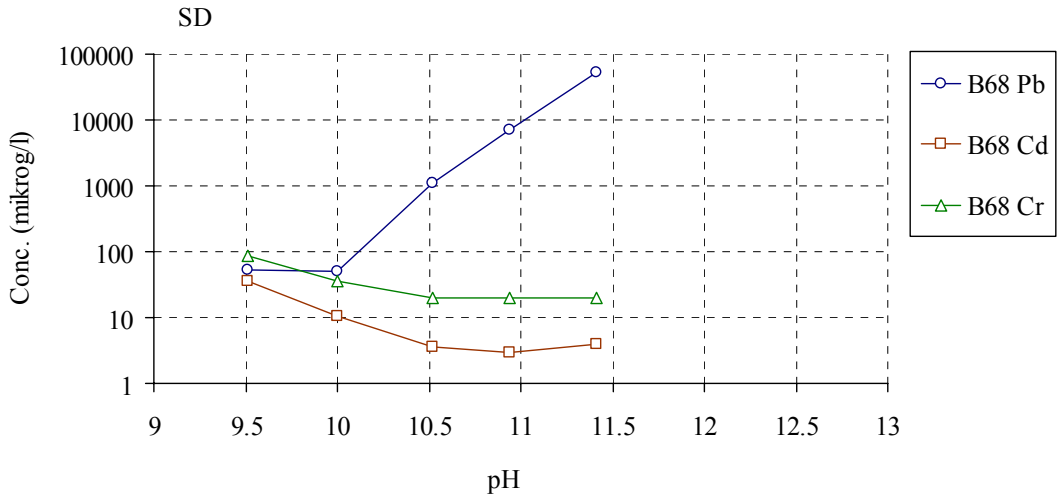

Figure 4.10. The concentrations of Pb, Cd and Cr in the wastewater as a function of the pH in the suspension during stepwise addition of H_2SO_4 in Ferrox-treatment of a semidry residue from Amagerforbrænding (SD).

4.9 Reaction time

The study of controlling and adjusting pH showed that it was possible to control the heavy-metal concentrations in the wastewater. In this study, the individual pH values

were maintained for approx. 10 minutes before sampling. Since, at the relevant pH level, the trace metals equilibrates, it is relevant to know whether equilibrium is obtained and for how long a given pH must be maintained in order for the wastewater to achieve the lowest trace metal content. This has been tested by Ferrox-treating a number of residues and reducing/controlling the pH to the values found to be the optimum in the previous study of the possibilities of pH control[8]. When the required pH is obtained, the sampling of the suspension begins at various intervals after the start of the pH reduction/control. The pH is, however, maintained constant. For the pH control is used either CO_2 aeration or addition of $FeSO_4$ or H_2SO_4. The samples are filtrated immediately after sampling, so that a sample reflects the wastewater at the given pH and time. The samples are analysed for Pb, Cd and Cr.

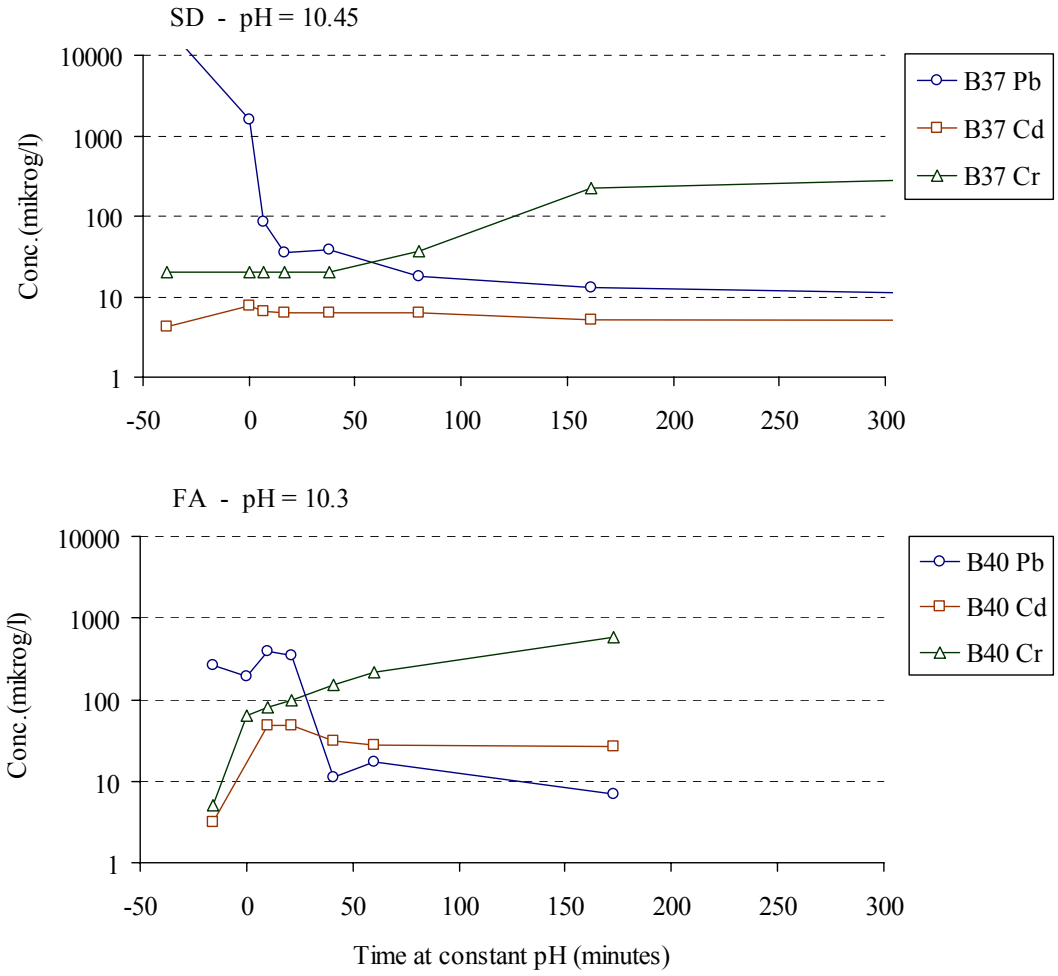

Figure 4.11. The content of Pb, Cd and Cr in the wastewater as a function of the time when the pH was maintained at a given level by means of CO_2. SD is the semidry residue from Amagerforbrænding and FA is fly ash from Vestforbrænding.

[8] Owing to lack of time and the consequent analytical deficiency, it has in several instances been necessary to choose a pH value for the kinetics tests without having all the analytical results from the pH control tests.

Figure 4.11 shows the content of Pb, Cd and Cr in the wastewater as a function of the time from which the pH was constant at pH reduction/control by means of CO_2 during treatment of residues from Amagerforbrænding and Vestforbrænding. It should be noted that the sampling began at the start of pH reduction/control by means of CO_2. Hence the negative times on Figure 4.11.

As seen from Figure 4.11, the Pb concentrations were initially very high, but fell rapidly. The Cr concentration rose in time and, except for a slight fall immediately after the required pH was reached, the Cd concentration was little dependent on the reaction time. The test of SD continued for 22 hours (i.e. far beyond what is shown in Figure 4.11), whereby Cr rose to over 1200 µg/l, while Pb and Cd remained at the same level. As shown in Figure 4.11, the result clearly shows that the reaction time is an important parameter. The choice of reaction time becomes a balancing of Pb, Cr and time consumption. With CO_2 as the pH-controlling additive, a reaction time of approx. 10 minutes at a maintained pH for SD and 20-40 minutes at a maintained pH for FA would seem appropriate. To this should be added the time it takes to adjust the process to the required pH, which in this case amounted to 39 minutes and 16 minutes for SD and FA respectively.

The result of the same test, but using concentrated sulphuric acid and $FeSO_4$ as pH-controlling additives on SD, FA and FA mixed with sludge, is shown in Figure 4.12. As is seen, Pb reacts more sluggishly at pH control by means of sulphuric acid during treatment of the SD residue. The Pb concentration did not fell to below 100 µg/l until 40 minutes had passed. To this should be added the 21 minutes it took to adjust the pH. For FA and FA mixed with sludge, the Pb concentration is below 100 µg/l after adjustment of the pH, which took 20 and 15 minutes respectively. The overall tendency is the same, i.e. an initial fall in the Pb concentration, a reasonably stable Cd concentration and a slow increase in the Cr concentration.

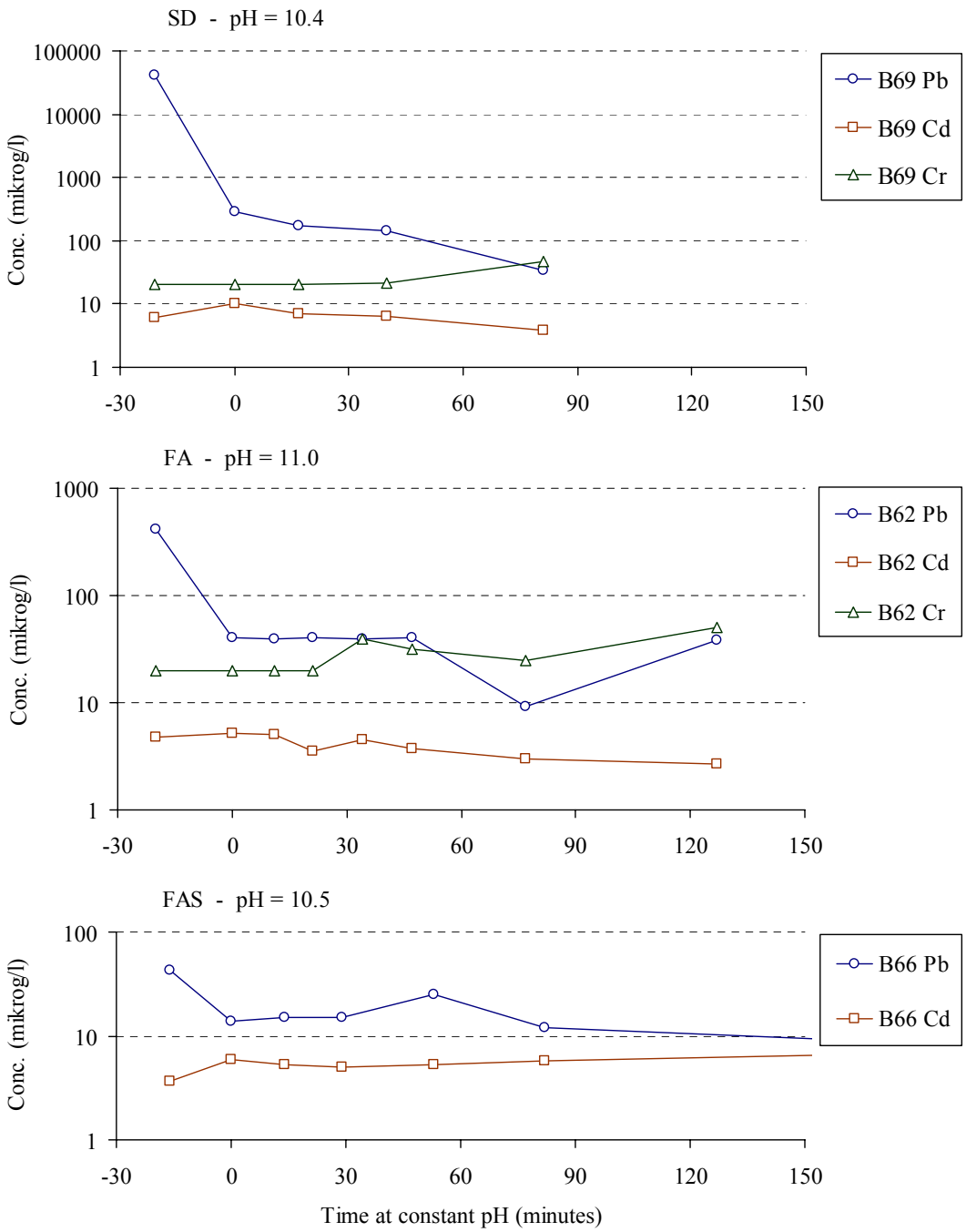

Figure 4.12. The content of Pb, Cd and Cr in the wastewater as a function of the period that the pH was maintained at a given level by means of sulphuric acid (SD) or ferrous sulphate (FA and FAS). SD is the semidry residue from Amagerforbrænding, FA is fly ash from Vestforbrænding and FAS is fly ash mixed with sludge from wet scrubbing at Vestforbrænding. Cr is not shown in the figure of FAS owing to the low chrome content of the wastewater during treatment of this residue.

4.10 Recirculation of the washwater

To reduce the water consumption, it is possible to recirculate the water that has been used for washing the Ferrox-product in the filter press into the process mixing cycle in the mixing tank. This method saves water amounting to approx. L/S 3 l/kg. In Batches B28-32 and B34-37 and B39, the possibilities of recirculation have been tested in five successive stabilisations of SD and FA respectively. The test was also aimed at determining how many batches have to be made in succession in order to reach a steady state, i.e. when the amounts of salts recirculated and removed reach a constant level.

The recirculation process is as follows: The washwater from the first stabilisation is recirculated for use as wastewater in the second stabilisation, whose washwater is recirculated for use as wastewater in the third stabilisation etc. On the face of it, one would expect the salt removal to be optimal in the first stabilisation, since fresh water is used for both mixing and washing. Then one would expect the salt removal to become slightly reduced and reach a constant level after a certain number of stabilisations.

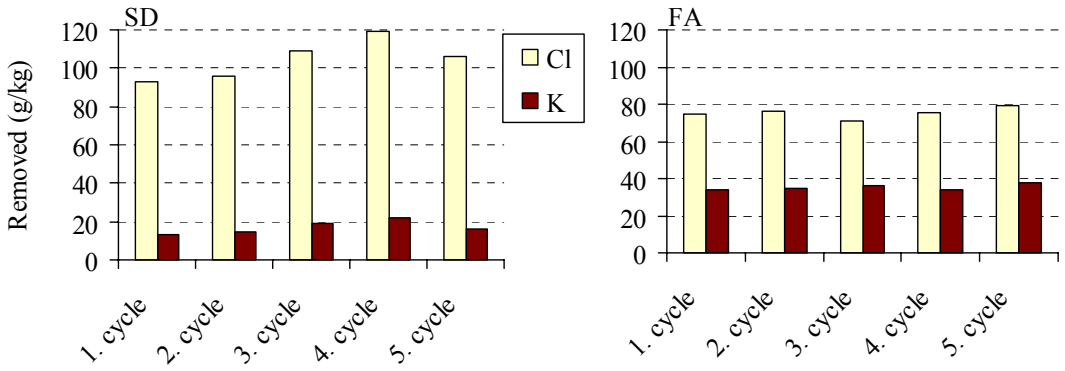

Figure 4.13. Total amounts of Cl and K removed by wastewater during Ferrox-treatment including recirculation. SD is the semidry residue from Amagerforbrænding and FA is fly ash from Vestforbrænding.

Figure 4.13 shows the total amount of salts removed for each of the five successive stabilisations including the salts added and removed by the washwater. The figure is based on the calculations in Appendix 24. From this will be seen that no more Cl or K is removed in the first stabilisation than in the following. The effect of recirculating the washwater is consequently no greater than the effect of the variations in the residues used for the individual batches and measurement uncertainties. Table 4.6 shows the result of a pH-static leaching at pH 9 and L/S 10 l/kg, and from this it is seen that the leaching of Cl and K does not increase as a result of recirculation of the washwater. This means that salt removal during the Ferrox-treatment does not decrease because the washwater is recirculated. Appendix 25 shows that the concentration of Cl and K in the wastewater is lower in the first stabilisation. The following stabilisations compensate for this, since an amount of Cl and K is removed during washing and recirculated so

that the total amount is reasonably uniform. This indicates that the removal of K and Cl is diffusion-controlled and not solubility-controlled. The experiment suggests that a steady state is reached after the second stabilisation.

Table 4.6. The result of pH-static leaching at pH 9 and L/S 10 l/kg for five successive stabilisations of SD and FA respectively. All values are stated in g/kg.

Residue	Element	1st batch	2nd batch	3rd batch	4th batch	5th batch
SD	Cl	4.1		2.3		1.7
	K	0.49		0.74		0.57
FA	Cl	1.5	1.5	1.7	1.5	1.6
	K	0.36	0.42	0.39	0.38	0.41

4.11 Reduced processing time

A test (B82) has been made on the FA residue, in which the Ferrox-suspension is pumped from the mixing tank into the process tank before the pH rises above 10, which would otherwise ensure precipitation of Fe^{2+} with OH^-. The wastewater from this had 23 µg/l Pb, 3 µg/l Cd and under 20 µg/l Cr. This is comparable to the result from the documentation of the process, so apparently it does not pose any problems that the last part of the Fe^{2+} precipitation takes place during aeration. The resultant Ferrox-product has not been leaching tested, but leaching tends not to be particularly sensitive to changes in the process configuration.

4.12 Subconclusion

Ferrox-treatments on a semiindustrial scale have been conducted in the installed pilot plant. The Ferrox-treatments comprise several batches of both a semidry APC-residue from Amagerforbrænding and fly ash from Vestforbrænding with and without sludge. In terms of process technology, the general functionality of the installed plant is good. The feeding system of the plant could not handle the FAS residue.

The most important resources of the Ferrox-treatment are the time consumption, the consumption of chemicals, and the consumption and discharge of water. The resource consumption depends on the type of residue being used.

A test of the sampling drawn from the filter press showed that there is a certain inhomogeneity in the produced material in terms of salts. This is probably due to the washing and related to the dehydration unit used.

Washing of FA-based Ferrox-products in the filter press by means of water equalling L/S 3 l/kg or L/S 4 l/kg for SD-based Ferrox-products removes the majority of the chloride salts. Washing at a higher L/S-ratio will probably not have any material effect on the leaching of salts from the finished Ferrox-product, since the leaching is subsequently diffusion-controlled or solubility-controlled. The washwater flow through the residue seems to be of no consequence and may therefore be chosen, taking into consideration other factors, such as time.

To achieve a 70 % oxidation of the iron(II) added to the Ferrox-product, oxidation/dispersion should take at least 15 minutes for FA-based Ferrox-products and 50 minutes for SD-based Ferrox-products. Further dispersion time only results in a marginally better oxidation of the iron(II).

It appears that the pH level controls the heavy-metal concentrations in the wastewater. Three different additives for pH adjustment and control have been tested. The three additives are CO_2, $FeSO_4$ and H_2SO_4. Based on the work pursued, the conclusion is that it will be necessary to control the pH of the wastewater, which has not been tested in the laboratory.

Table 4.7 shows the pH-values of the individual residues and additives that produced the best wastewater quality in terms of Pb, Cd and Cr.

Table 4.7. Summary of the pH-control tests. Recommended pH of the wastewater during treatment of various residues with various additives for pH adjustment/control.

	CO_2	$FeSO_4$	H_2SO_4
SD	10.3	10.4	10-10.5
FA	10.7	11.0	-
FAS	11.0	10.5	-

It has been tested whether the time that the suspension stays at maintained pH is significant. The result was that this is of great importance to the Pb and Cr concentrations in the wastewater. The optimum reaction time at pH control by means of CO_2, $FeSO_4$ and H_2SO_4 was subsequently identified. The result is shown in Table 4.8. As the definite reaction time for FA and FAS, 30 minutes are recommended, to ensure that the Pb concentration has decreased. For SD, 60 minutes are recommended.

Table 4.8. Summary of reaction time tests. The recommended reaction time from start of pH adjustment/control during treatment of various residues by means of different additives for pH adjustment/control. All values are stated in minutes.

	CO_2	$FeSO_4$	H_2SO_4
SD	50	-	60
FA	40	20	-
FAS	-	15	-

The result of the examination of the reaction time confirms that the pH-values found during treatment of SD and FA, i.e. 10.4 and 11.0 respectively, are correct, if H_2SO_4 or $FeSO_4$ is added However, the reaction time test of fly ash mixed with sludge showed that the pH found was too low, since the Pb concentrations were generally very low and the Cd concentrations high. A comparison with the curves of the various pH control tests indicates that a pH around 10.8 is better.

Recirculation of the washwater has been tested. These tests showed that at least two successive stabilisations must be made to reach a steady state. To document the process, at least three stabilisations should be made to prove that a steady state has been reached. The tests also showed that the salt removal was not reduced by recirculation of the washwater.

All the tests of process parameters are summed up in Table 4.9, which contains the optimised parameter values used to document the Ferrox-process in the pilot plant.

Table 4.9. Process parameters for optimised stabilisation of residues in the pilot scale plant.

Residue	SD	FA	FAS
Residue, quantity	160 kg	175 kg	175 kg (TS)
Fe amount (weight Fe/weight res.)	4.9 %	1.25 %	1.25 %
Aeration time	50 min.	20 min.	20 min.
pH controller	sulphuric acid	ferrous sulphate	ferrous sulphate
Optimum pH	10.4[1)]	11.0	10.8
Reaction time[2)]	60 min.	30 min.	30 min.
Washing L/S	4 l/kg	3 l/kg	3 l/kg
Min. successive stabilisations	3	3	3

[1)] 10.3, if the temperature is above 40 °C.

[2)] Measured from the start of pH adjustment.